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ACTIVE-ENERGY-RAY-CURABLE PRESSURE-SENSITIVE ADHESIVE COMPOSITION

Abstract:

PROBLEM TO BE SOLVED: To obtain a pressure-sensitive adhesion composition which is curable by active energy rays such as ultraviolet rays, especially a pressure-sensitive adhesive composition which is useful for protective films for articles made of various substrates such as paper, plastic boards, metals, and glass, for protective films for automotive bodies, and for pressure-sensitive adhesive sheet for temporary bonding.

SOLUTION: This pressure-sensitive adhesive composition contains a polyisocyanate derivative [A] and an ethylenically unsaturated monomer [B]. The polyisocyanate derivative [A] is prepared by reacting isocyanate groups of an isocyanate-group-containing compound [a] prepared by the reaction of a polyol (a1) with a polyisocyanate (a2) with the hydroxyl group of a hydroxyl-group-containing (meth)acrylate (a3) and the hydroxyl group of a saturated alcohol (a4) so as to form urethane bonds.

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(54)【発明の名称】 活性エネルギー線硬化型粘着剤組成物

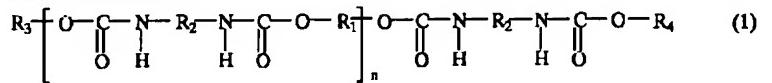
(57)【要約】

【課題】 紫外線等の活性エネルギー線で硬化する粘着剤組成物、特に紙、プラスチック板、金属、ガラス等の各種基材からなる物品の保護フィルム用途や自動車ボディ用の保護フィルム用途、或いは仮接着用の粘着シートに有用な活性エネルギー線硬化型粘着剤組成物を提供すること。

【解決手段】 ポリオール〔a1〕とポリイソシアネート〔a2〕との反応物であるイソシアネート基含有化合物〔a〕中のイソシアネート基が、水酸基含有(メタ)アクリレート〔a3〕の水酸基及び、飽和アルコール〔a4〕の水酸基と、それぞれウレタン結合を形成してなるポリイソシアネート系誘導体〔A〕、及びエチレン性不飽和单量体〔B〕を含有してなる活性エネルギー線硬化型粘着剤組成物。

【特許請求の範囲】

【請求項1】 ポリオール(a1)とポリイソシアネート(a2)との反応物であるイソシアネート基含有化合物[a]中のイソシアネート基が、水酸基含有(メタ)アクリレート(a3)の水酸基及び、飽和アルコール(a4)の水酸基と、それぞれウレタン結合を形成してなるポリイソシアネート系誘導体[A]、及びエチレン性不飽和单量体[B]を含有してなることを特徴とする活性エネルギー線硬化型粘着剤組成物。



ここで、R₁はポリオール(a1)の両端ウレタン結合残基、R₂はポリイソシアネート(a2)の両端ウレタン結合残基、R₃は水酸基含有(メタ)アクリレート(a3)のウレタン結合残基、R₄は飽和アルコール(a4)のウレタン結合残基で、nは1以上の整数である。

【請求項4】 一般式(1)で示されるポリイソシアネート系誘導体[A]のnが1～15であることを特徴とする請求項3記載の活性エネルギー線硬化型粘着剤組成物。

【請求項5】 ポリオール(a1)が水添ポリブタジエンポリオールであることを特徴とする請求項1～4いずれか記載の活性エネルギー線硬化型粘着剤組成物。

【請求項6】 エチレン性不飽和单量体[B]が、炭素数6以上の脂肪族又は脂環族アルキル(メタ)アクリレートであることを特徴とする請求項1～5いずれか記載の活性エネルギー線硬化型粘着剤組成物。

【請求項7】 更に、光重合開始剤[C]を含有することを特徴とする請求項1～6いずれか記載の活性エネルギー線硬化型粘着剤組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、紫外線等の活性エネルギー線で硬化し粘着機能を発現する粘着剤組成物、特には紙、プラスチック板、金属、ガラス等の各種基材からなる物品の保護フィルム用途や自動車ボディ用の保護フィルム用途、或いは仮接着用の粘着シートに有用な活性エネルギー線硬化型粘着剤組成物に関するものである。

【0002】

【従来の技術】近年、紙、プラスチック板、金属、ガラス等の各種基材からなる物品や自動車ボディ等の保護フィルムに用いる粘着剤としては、粘着物性に優れる他、屋外での保管等に適用できるように耐候性も必要とされる。従来より、かかる粘着剤としてはアクリル系樹脂やゴム系樹脂が多用されているが、基材との密着性や耐候性とのバランスの点で一長一短があり、その改善が必要である。また、従来のアクリル系樹脂やゴム系樹脂は通

【請求項2】 ポリイソシアネート系誘導体[A]1分子中のエチレン性不飽和基数が1～3個であること特徴とする請求項1記載の活性エネルギー線硬化型粘着剤組成物。

【請求項3】 ポリイソシアネート系誘導体[A]が、下記一般式(1)で示される構造であることを特徴とする請求項1又は2記載の活性エネルギー線硬化型粘着剤組成物。

【化1】

常溶剤型のものであるため、環境問題の点からも対応の余地がある。

【0003】一方、ごく短時間の紫外線等の照射により硬化が完了するという優位性から、活性エネルギー線硬化型の粘着剤あるいは接着剤の検討がなされている。例えば、特開平6-184498号公報では、(メタ)アクリル酸及びカルボキシル含有(メタ)アクリレートからなる群から選ばれた少なくとも1種とポリウレタンポリ(メタ)アクリレートからなる硬化型接着剤組成物が開示されている。かかる接着剤組成物は、電子線硬化することにより、フィルムに対する接着強度が発揮され、ラミネート用接着剤として用いられることが開示されている。

【0004】また、特開平11-189762号公報では、ポリエステルポリオールとポリイソシアネート及びモノヒドロキシアルキルアクリレートからなるウレタンアクリレートと反応性希釈剤からなる樹脂組成物が粘着シート基材用樹脂組成物として用いられることが開示されている。更に、特開平4-183770号公報では、水添ポリブタジエンポリオールとポリイソシアネートの反応物中の水酸基にアクリレートを反応させて得られるウレタン(メタ)アクリレートオリゴマーと単官能(メタ)アクリレートを含有してなる放射線硬化型粘着剤組成物が開示されている。

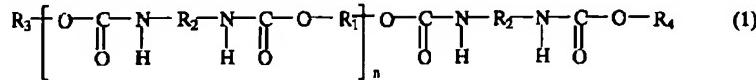
【0005】

【発明が解決しようとする課題】そこで本発明者等は、上記公報開示技術も含めてこれまで知られている活性エネルギー線硬化型の樹脂組成物を、上記の保護フィルム用粘着剤に適用すべく検討を行ったが、基材との接着性と耐候性とのバランスがほどよく取れたものではなく、その開発が望まれているところである。本発明ではこのような背景において、基材との接着性と耐候性のバランスに優れ、各種保護フィルムに用いる粘着剤として有用な活性エネルギー線硬化型粘着剤組成物を提供することを目的とするものである。

【0006】

【課題を解決するための手段】しかるに本発明者等は、かかる事情に鑑み鋭意研究を重ねた結果、ポリオール

(a1) とポリイソシアネート (a2) との反応物であるイソシアネート基含有化合物 [a] 中のイソシアネート基が、水酸基含有 (メタ) アクリレート (a3) の水酸基及び、飽和アルコール (a4) の水酸基と、それぞれウレタン結合を形成してなるポリイソシアネート系誘導体 [A]、及びエチレン請求項不飽和单量体 [B] を含有してなる活性エネルギー線硬化型粘着剤組成物がある。



ここで、R₁ はポリオール (a1) の両端ウレタン結合残基、R₂ はポリイソシアネート (a2) の両端ウレタン結合残基、R₃ は水酸基含有 (メタ) アクリレート (a3) のウレタン結合残基、R₄ は飽和アルコール (a4) のウレタン結合残基で、n は 1 以上の整数である。

【0009】また本発明では、ポリオール (a1) が水添ポリブタジエンポリオールであるとき、エチレン性不飽和单量体 [B] が、炭素数 6 以上の脂肪族又は脂環族アルキル (メタ) アクリレートであるとき、本発明の効果を顕著に發揮する。

【0010】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明で用いられるポリイソシアネート系誘導体 [A] は、ポリオール (a1) とポリイソシアネート (a2) との反応物であるイソシアネート基含有化合物 [a] 中のイソシアネート基が、水酸基含有 (メタ) アクリレート (a3) の水酸基及び、飽和アルコール (a4) の水酸基と、それぞれウレタン結合を形成してなるポリイソシアネート系誘導体であり、該ポリイソシアネート系誘導体 [A] を構成する各成分について以下に説明する。

【0011】ポリオール (a1) としては、特に限定されず、例えば、エチレングリコール、ジエチレングリコール、トリエチレングリコール、テトラエチレングリコール、ポリエチレングリコール、プロピレングリコール、ジプロピレングリコール、ポリプロピレングリコール、ブチレングリコール、1, 4-ブタンジオール、ポリブチレングリコール、1, 6-ヘキサンジオール、オオベンチルグリコール、シクロヘキサンジメタノール、水素添加ビスフェノール A、ポリカプロラクトン、トリメチロールエタン、トリメチロールプロパン、ポリトリメチロールプロパン、ベンタエリスリトール、ポリベンタエリスリトール、ソルビトール、マンニトール、アラビトール、キシリトール、ガラクトトール、グリセリン、ポリグリセリン、ポリテトラメチレングリコール、水添ポリブタジエンポリオール等の多価アルコールや、ポリエチレンオキサイド、ポリプロピレンオキサイド、エチレンオキサイド/プロピレンオキサイドのブロック又はランダム共重合の少なくとも 1 種の構造を有するポリエーテルポリオール、該多価アルコール又はポリエー

上記目的に合致することを見出し、本発明を完成した。

【0007】本発明では、特にポリイソシアネート系誘導体 [A] が、下記一般式 (1) で示される構造であることが、活性エネルギー線照射による硬化被膜の高接着性の点で好ましい。

【0008】

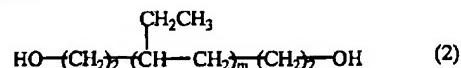
【化2】

テルポリオールと無水マレイン酸、マレイン酸、フマル酸、無水イタコン酸、イタコン酸、アジピン酸、イソフタル酸等の多塩基酸との縮合物であるポリエステルポリオール、カプロラクトン変性ポリテトラメチレンポリオール等のカプロラクトン変性ポリオール、ポリオレフィン系ポリオール等が挙げられ、更には、2, 2-ビス(ヒドロキシメチル) 酪酸、酒石酸、2, 4-ジヒドロキシ安息香酸、3, 5-ジヒドロキシ安息香酸、2, 2-ビス(ヒドロキシメチル) プロピオン酸、2, 2-ビス(ヒドロキシエチル) プロピオン酸、2, 2-ビス(ヒドロキシプロピル) プロピオン酸、ジヒドロキシメチル酢酸、ビス(4-ヒドロキシフェニル) 酢酸、4, 4-ビス(4-ヒドロキシフェニル) ペンタン酸、ホモゲンチジン酸等のカルボキシル基含有ポリオールや、1, 4-ブタンジオールスルホン酸ナトリウム等のスルホン酸基又はスルホン酸塩基含有ポリオール等も挙げられ、1 種または 2 種以上併用して用いられる。上記ポリオール (a1) の中でも、特に水添ポリブタジエンポリオールが耐候性や耐水性の点で好ましく用いられる。

【0012】かかる水添ポリブタジエンポリオールは、下記一般式 (2) で示されるもので、その分子量が 300~6000、好ましくは 500~3000 のものが有用である。また、ヨウ素価は 0~50、好ましくは 0~20 で、水酸基価は 15~400 mg KOH/g、好ましくは 30~250 mg KOH/g が適当である。

【0013】

【化3】



ここで、m は 3~110 の整数である。

【0014】ポリイソシアネート (a2) としては、特に限定されることなく、例えば芳香族系、脂肪族系、脂環式系等のポリイソシアネートが挙げられ、中でもトリレンジイソシアネート、ジフェニルメタンジイソシアネート、水添化ジフェニルメタンジイソシアネート、変性ジフェニルメタンジイソシアネート、水添化キシリレンジイソシアネート、キシリレンジイソシアネート、ヘキサメチレンジイソシアネート、トリメチルヘキサメチレンジイソシアネート、テトラメチルキシリレンジイソシアネート、テトラメチルキシリレンジイソシ

アネート、イソホロンジイソシアネート、ノルボルネンジイソシアネート、1, 3-ビス(イソシアナトメチル)シクロヘキサン等のジイソシアネート或いはこれらの3量体、ビューレット型ポリイソシアネート等が好適に用いられる。該ポリイソシアネート化合物(a2)の分子量は、水酸基との反応性の点から150~700が好ましい。

【0015】水酸基含有(メタ)アクリレート(a3)としては、特に限定されることなく、例えば、2-ヒドロキシエチル(メタ)アクリレート、2-ヒドロキシプロピル(メタ)アクリレート、2-ヒドロキシブチル(メタ)アクリレート、2-ヒドロキシエチルアクリロイルホスフェート、4-ブチルヒドロキシ(メタ)アクリレート、2-(メタ)アクリロイロキシエチル-2-ヒドロキシプロピルフタレート、グリセリンジ(メタ)アクリレート、2-ヒドロキシ-3-アクリロイロキシプロピル(メタ)アクリレート、カプロラクトン変性2-ヒドロキシエチル(メタ)アクリレート、ペンタエリスリトールトリ(メタ)アクリレート、ジペンタエリスリトールペンタ(メタ)アクリレート、カプロラクトン変性2-ヒドロキシエチル(メタ)アクリレート等が挙げられる。これらの中でもアルキル基の炭素数が2~20の水酸基含有(メタ)アクリレートが粘着性、耐候性の点で有用である。

【0016】飽和アルコール(a4)としては、特に限定されることなく、例えば、アルキルモノアルコール(メタノール、エタノール、n-プロピルアルコール、イソプロピルアルコール、ヘキサノール、デカノール、ラウリルアルコール、ステアリルアルコール、ベヘニルアルコール等、炭素1~22のアルコール)、エチレングリコールモノアルキルエーテル、ジエチレングリコールモノアルキルエーテル、プロピレングリコールモノアルキルエーテル、ポリプロピレングリコールモノアルキルエーテル等が挙げられ、中でもアルキルモノアルコール、特にはメタノール、エタノール、n-プロピルアルコール、イソプロピルアルコール等が好適である。

【0017】本発明で用いられるポリイソシアネート系誘導体[A]は、反応制御の安定性と製造時間の短縮の観点から、ポリオール(a1)とポリイソシアネート(a2)を反応させて、イソシアネート基含有化合物[a]を得た後、次いで該イソシアネート基含有化合物[a]中のイソシアネート基が、水酸基含有(メタ)アクリレート(a3)の水酸基及び、飽和アルコール(a4)の水酸基と、それぞれウレタン結合を形成することにより得られる。

【0018】例えば、イソシアネート基含有化合物[a]が2個のイソシアネート基を有する場合では、1個のイソシアネート基が水酸基含有(メタ)アクリレート(a3)の水酸基とウレタン結合を形成し、残りの1個のイソシアネート基が飽和アルコール(a4)の水酸

基とウレタン結合を形成したポリイソシアネート系誘導体[A]となり、イソシアネート基含有化合物[a]が3個のイソシアネート基を有する場合では、1個のイソシアネート基が水酸基含有(メタ)アクリレート(a3)(または飽和アルコール(a4))の水酸基とウレタン結合を形成し、残りの2個のイソシアネート基が飽和アルコール(a4)(または水酸基含有(メタ)アクリレート(a3))の水酸基とウレタン結合を形成したポリイソシアネート系誘導体[A]となる。

【0019】上記ウレタン結合を形成する反応を行うに当たっては、特に限定されず、(イ)イソシアネート基含有化合物[a]中に、水酸基含有(メタ)アクリレート(a3)及び飽和アルコール(a4)を一括に仕込み反応させる方法、(ロ)イソシアネート基含有化合物[a]と水酸基含有(メタ)アクリレート(a3)を反応させた後、飽和アルコール(a4)を反応させる方法、(ハ)イソシアネート基含有化合物[a]と飽和アルコール(a4)を反応させた後、水酸基含有(メタ)アクリレート(a3)を反応させる方法、が挙げられるが、反応制御の安定性と製造時間の短縮の観点から、(ロ)の方法が好ましい。

【0020】また、かかる反応においては、反応を促進する目的でジブチルチンジラウレート等の触媒を用いることも好ましく、更に反応温度は30~90℃、特に40~70℃の範囲が好ましい。

【0021】本発明では、上記ポリイソシアネート系誘導体[A]の中でも、上記一般式(1)で示される構造であることが高接着性の点で好ましく、特には、一般式(1)で示されるポリイソシアネート系誘導体のnが1~15、更には1~10であることが好ましい。

【0022】かかる一般式(1)で示されるポリイソシアネート系誘導体を得るに当たっては特に、ポリオール(a1)とポリイソシアネート(a2)をk:k+1(モル比)(kは1以上の整数である。)の反応モル比で反応させ、イソシアネート基含有化合物[a]を得た後、該イソシアネート基含有化合物[a]に水酸基含有(メタ)アクリレート(a3)を1:1の反応モル比で反応させ、更に得られた反応生成物に飽和アルコール(a4)を1:1の反応モル比で反応させる方法、或いは、該イソシアネート基含有化合物[a]に飽和アルコール(a4)を1:1の反応モル比で反応させ、更に得られた反応生成物に水酸基含有(メタ)アクリレート(a3)を1:1の反応モル比で反応させる方法が好ましい。中でも反応制御の安定性と製造時間の短縮の観点から前者の方法が好ましく用いられる。

【0023】また、上記ポリイソシアネート系誘導体[A]の製造において、得られるポリイソシアネート系誘導体[A]が高粘度となる場合は、必要に応じて反応缶にあらかじめ後述のエチレン性不飽和单量体[B]を仕込み、エチレン性不飽和单量体[B]中で各成分を反

応させポリイソシアネート系誘導体【A】を製造することもできる。

【0024】かくして本発明で用いられるポリイソシアネート系誘導体【A】が得られるが、本発明ではポリイソシアネート系誘導体【A】の重量平均分子量が5,000～100,000であることが好ましく、更には10,000～50,000であることが好ましい。かかる重量平均分子量が5,000未満では粘着性が低くなり、100,000を越えると塗工性が悪くなり好ましくない。

【0025】尚、上記の重量平均分子量とは、標準ポリスチレン分子量換算による重量平均分子量であり、高速液体クロマトグラフィー（昭和電工社製、「Shodex GPC system-11型」）に、カラム：Shodex GPC KF-806L（排除限界分子量：2×10⁷、分離範囲：100～2×10⁷、理論段数：10,000段／本、充填剤材質：スチレンジビニルベンゼン共重合体、充填剤粒径：10μm）の3本直列を用いることにより測定される。

【0026】また、ポリイソシアネート系誘導体【A】のガラス転移温度〔TMA（熱機械的分析）法により測定〕としては、0℃以下が好ましく、更には-20℃以下が好ましい。0℃を越えると硬化収縮が大きく、粘着性が低くなり好ましくない。更に、本発明では、ポリイソシアネート系誘導体【A】1分子中のエチレン性不飽和基数が1～3個であることが好ましく、3個を越えると活性エネルギー線照射による硬化被膜の接着性が低下することとなり好ましくない。

【0027】本発明で用いられるエチレン性不飽和單量体【B】としては、特に限定されず、单官能（メタ）アクリレート、2官能（メタ）アクリレート、3官能以上の（メタ）アクリレート等が挙げられ、中でも接着性の点から单官能（メタ）アクリレートが有効であり、特に炭素数6以上の脂肪族又は脂環族アルキル（メタ）アクリレートが好ましい。

【0028】炭素数6以上の脂肪族又は脂環族アルキル（メタ）アクリレートとしては、例えばヘキシル（メタ）アクリレート、ヘプチル（メタ）アクリレート、オクチル（メタ）アクリレート、ノニル（メタ）アクリレート、デシル（メタ）アクリレート、イソデシル（メタ）アクリレート、ドデシル（メタ）アクリレート、ステアリル（メタ）アクリレート、ラウリル（メタ）アクリレート、シクロヘキシル（メタ）アクリレート、イソボルニル（メタ）アクリレート、ジクロペンテニル（メタ）アクリレート、トリシクロデカニル（メタ）アクリレート等が挙げられ、中でもイソデシル（メタ）アクリレート、ラウリル（メタ）アクリレート、シクロヘキシル（メタ）アクリレートが好適に用いられる。

【0029】炭素数6以上の脂肪族又は脂環族アルキル（メタ）アクリレート以外の单官能（メタ）アクリレ-

トとしては、例えばメチル（メタ）アクリレート、エチル（メタ）アクリレート、フェノキシエチル（メタ）アクリレート、グリセリンモノ（メタ）アクリレート、グリシジル（メタ）アクリレート、ジシクロペンテニル（メタ）アクリレート、n-ブチル（メタ）アクリレート、ベンジル（メタ）アクリレート、フェノールエチレンオキサイド変性（n=2）（メタ）アクリレート、ノニルフェノールプロビレンオキサイド変性（n=2.5）（メタ）アクリレート、2-（メタ）アクリロイルオキシエチルアシッドホスフェート、フルフリル（メタ）アクリレート、カルビトール（メタ）アクリレート、ベンジル（メタ）アクリレート、ブトキシエチル（メタ）アクリレート、アリル（メタ）アクリレート、2-ヒドロキシエチル（メタ）アクリレート、2-ヒドロキシプロピル（メタ）アクリレート、2-ヒドロキシブチル（メタ）アクリレート、2-フェノキシ-2-ヒドロキシプロピル（メタ）アクリレート、2-ヒドロキシ-3-フェノキシプロピル（メタ）アクリレート、3-クロロ-2-ヒドロキシプロピル（メタ）アクリレート等が挙げられる。これらの中でも、水酸基を含有しない单官能（メタ）アクリレートが好ましく、更には、分子量が100～300程度の該アクリレートが好ましい。

【0030】2官能（メタ）アクリレートとしては、例えば、エチレングリコールジ（メタ）アクリレート、ジエチレングリコールジ（メタ）アクリレート、テトラエチレングリコールジ（メタ）アクリレート、ポリエチレングリコールジ（メタ）アクリレート、プロピレングリコールジ（メタ）アクリレート、ジプロピレングリコールジ（メタ）アクリレート、ポリプロピレングリコールジ（メタ）アクリレート、ブチレングリコールジ（メタ）アクリレート、ネオペンチルグリコールジ（メタ）アクリレート、エチレンオキサイド変性ビスフェノールA型ジ（メタ）アクリレート、プロピレンオキサイド変性ビスフェノールA型ジ（メタ）アクリレート、1,6-ヘキサンジオールジ（メタ）アクリレート、グリセリンジ（メタ）アクリレート、ペンタエリスリトールジ（メタ）アクリレート、エチレングリコールジグリシジルエーテルジ（メタ）アクリレート、ジエチレングリコールジグリシジルエーテルジ（メタ）アクリレート、フタル酸ジグリシジルエステルジ（メタ）アクリレート、ヒドロキシビバリン酸変性ネオペンチルグリコールジ（メタ）アクリレート等が挙げられる。

【0031】3官能以上の（メタ）アクリレートとしては、例えば、トリメチロールプロパントリ（メタ）アクリレート、ペンタエリスリトールトリ（メタ）アクリレート、ペンタエリスリトールトライ（メタ）アクリレート、ジペンタエリスリトールベンタ（メタ）アクリレート、ジペンタエリスリトールヘキサ（メタ）アクリレート、トリ（メタ）アクリロイルオキシエトキシトリメチ

ロールプロパン、グリセリンポリグリシジルエーテルボリ(メタ)アクリレート等が挙げられる。

【0032】また、エチレン性不飽和单量体[B]として、上記の他にアクリル酸のミカエル付加物或いは2-アクリロイルオキシエチルジカルボン酸モノエステルも挙げられる。

【0033】アクリル酸のミカエル付加物としては、アクリル酸ダイマー〔下記(3)式〕、メタクリル酸ダイマー、アクリル酸トリマー〔下記(4)式〕、メタクリル酸トリマー、アクリル酸テトラマー〔下記(5)式〕、メタクリル酸テトラマー等が挙げられる、中でもアクリル酸ダイマーが好ましい。

【0034】

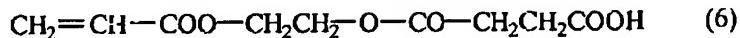
【化4】



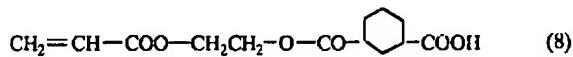
【化5】



【化8】



【化9】



【化10】



【0037】上記エチレン性不飽和单量体[B]は、單独で用いてもまたは2種以上併用して用いてもよい。

【0038】また本発明において、上記ポリイソシアネート系誘導体[A]とエチレン性不飽和单量体[B]の含有量については、[A] : [B] が 10 : 90 ~ 95 : 5 (重量比) であることが好ましく、更には 50 : 50 ~ 80 : 20 (重量比) であることが好ましい。ポリイソシアネート系誘導体[A]の含有量が上記範囲未満では密着性が悪くなり、一方上記範囲を越えると塗工性が悪くなり、実用上問題が起こり好ましくない。

【0039】本発明では、更に光重合開始剤[C]を併用することが好ましく、該光重合開始剤[C]としては、光の作用によりラジカルを発生するものであれば特に限定されず、具体的には、4-フェノキシジクロロアセトフェノン、4-t-ブチルジクロロアセトフェノン、ジエトキシアセトフェノン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-オン、1-(4-イソプロピレンフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン、1-(4-ドデシルフェニル)-2-ヒドロキシ-2-メチルプロパン-1-オン、4-(2-ヒドロキシエトキシ)-フェニル(2-ヒドロ

【化6】



【0035】また、2-アクリロイルオキシエチルジカルボン酸モノエステルとは、特定の置換基をもつカルボン酸であり、例えば2-アクリロイルオキシエチルコハク酸モノエステル〔下記(6)式〕、2-メタクリロイルオキシエチルコハク酸モノエステル、2-アクリロイルオキシエチルフタル酸モノエステル〔下記(7)式〕、2-メタクリロイルオキシエチルフタル酸モノエステル、2-アクリロイルオキシエチルヘキサヒドロフタル酸モノエステル〔下記(8)式〕、2-メタクリロイルオキシエチルヘキサヒドロフタル酸モノエステル等が挙げられ、好ましくは2-アクリロイルオキシエチルヘキサヒドロフタル酸モノエステルである。更に、その他オリゴエステルアクリレート〔下記(9)式〕も挙げができる。

【0036】

【化7】

キシ-2-プロピル)ケトン、1-ヒドロキシシクロヘキシルフェニルケトン、2-メチル-1-[4-(メチルチオ)フェニル]-2-モルホリノプロパン-1、ベンゾイン、ベンゾインメチルエーテル、ベンゾインエチルエーテル、ベンゾインイソプロピルエーテル、ベンゾインイソブチルエーテル、ベンジルジメチルケタール、ベンゾフェノン、ベンゾイル安息香酸、ベンゾイル安息香酸メチル、4-フェニルベンゾフェノン、ヒドロキベンゾフェノン、4-ベンゾイル-4'-メチルジフェニルサルファイド、3, 3'-ジメチル-4-メキシベンゾフェノン、チオキサンソン、2-クロルチオキサンソン、2-メチルチオキサンソン、2, 4-ジメチルチオキサンソン、イソプロピルチオキサンソン、カンフアーキノン、ジベンゾスペロン、2-エチルアンスラキノン、4', 4''-ジエチルイソフタロフェノン、3, 3', 4, 4'-テトラ(t-ブチルパーオキシカルボニル)ベンゾフェノン、α-アシロキシムエステル、アシルホスフィンオキサイド、メチルフェニルグリオキシレート、ベンジル、9, 10-フェナヌスレンキノン、4-(2-ヒドロキシエトキシ)フェニル-(2-ヒドロキシ-2-プロピル)ケトン等が挙げられ、中でもベ

シジルジメチルケタール、1-ヒドロキシクロヘキシリフェニルケトン、ベンゾイルイソプロピルエーテル、4-(2-ヒドロキシエトキシ)-フェニル(2-ヒドロキシ-2-プロピル)ケトン、2-ヒドロキシ-2-メチル-1-フェニルプロパン-1-オンが好適に用いられる。

【0040】かかる光重合開始剤[C]の配合量については、ポリイソシアネート系誘導体[A]とエチレン性不飽和单量体[B]の合計100重量部に対して、1~10重量部であることが好ましく、より好ましくは2~5重量部である。かかる配合量が1重量部未満では紫外線硬化の場合の硬化速度が極めて遅くなり、10重量部を越えても硬化性は向上せず無駄である。

【0041】更に、必要に応じて、光重合開始剤の助剤としてトリエタノールアミン、トリイソプロパノールアミン、4,4'-ジメチルアミノベンゾフェノン(ミヒラーケトン)、4,4'-ジエチルアミノベンゾフェノン、2-ジメチルアミノエチル安息香酸、4-ジメチルアミノ安息香酸エチル、4-ジメチルアミノ安息香酸(n-ブトキシ)エチル、4-ジメチルアミノ安息香酸イソアミル、4-ジメチルアミノ安息香酸2-エチルヘキシル、2,4-ジエチルチオキサンソン、2,4-ジイソプロピルチオキサンソン等を併用することも可能である。

【0042】また、上記のポリイソシアネート系誘導体[A]、エチレン性不飽和单量体[B]、光重合開始剤[C]以外にも、酸化防止剤、難燃剤、帶電防止剤、充填剤、レベリング剤、安定剤、補強剤、艶消し剤等を配合することも可能である。更に、架橋剤として、熱により架橋を引き起す作用をもつ化合物、具体的にはエボキシ化合物、アジリシン化合物、メラミン化合物、イソシアネート化合物、キレート化合物等も使用できる。

【0043】また、粘着付与性化合物として、ロジン類、ロジンエステル化合物、ビネン系ポリマー、水添石油樹脂、炭化水素樹脂、ソルビタン脂肪酸エステル、ポリオキシエチレンソルビタン脂肪酸エステル、3-メチルペンタン-1,3,5-トリオール等の添加も差し支えない。

【0044】また、溶剤も適宜配合することができ、かかる溶剤としては酢酸エチル、トルエン、キシレン、メタノール、エタノール、ブタノール、アセトン、メチルイソブチルケトン、メチルエチルケトン、セロソルブ類、ジアセトニアルコール等が挙げられ、ポリイソシアネート系誘導体[A]とエチレン性不飽和单量体[B]の合計量に対して、1~50重量%程度添加することができる。

【0045】本発明の粘着剤組成物は、通常基材シート等に塗布されて粘着シートや粘着テープ等として実用に供されることが多く、基材に塗布後、活性エネルギー線照射によって硬化され粘着性が発現させられる。

【0046】塗布する基材としては、ポリ塩化ビニル、ポリブテン、ポリブタジエン、ポリウレタン、エチレン-酢酸ビニル共重合体、ポリエチレンテレフタレート、ポリエチレン、ポリビロビレン、エチレン-プロピレン共重合体、ポリメチルペンテン、ポリブチレンテレフタレート等の透明フィルムが挙げられ、特に自動車ボディの塗膜の保護フィルム用途にはポリエチレンフィルムや、耐候剤やその他の添加剤が配合されたポリエチレンフィルム等が、半導体ウエハのバックグランド工程での凹凸面の表面保護用途や、ダイシング工程での、エキスパンドが必要な用途に用いる場合には、柔軟性、延伸性に優れるポリ塩化ビニル、ポリエチレン、ポリブロビレン、エチレン-プロピレン共重合体、エチレン-酢酸ビニル共重合体等の透明或いは活性エネルギー線透過が可能な着色フィルムが好適に用いられる。

【0047】該活性エネルギー線としては、遠紫外線、紫外線、近紫外線、赤外線等の光線、X線、 γ 線等の電磁波の他、電子線、プロトン線、中性子線等が利用できるが、硬化速度、照射装置の入手のし易さ、価格等から紫外線照射による硬化が有利である。また、活性エネルギー線照射に統して80~200°C程度の温度で加熱処理することもできる。

【0048】紫外線照射により硬化させる方法としては、150~450nm波長域の光を発する高圧水銀ランプ、超高圧水銀灯、カーボンアーク灯、メタルハライドランプ、キセノンランプ、ケミカルランプ等を用いて、100~4000mJ/cm²程度、好ましくは100~3000mJ/cm²程度照射すればよい。

【0049】本発明の活性エネルギー線硬化型粘着剤組成物は再剥離性を有しているので、金属板、ガラス板、プラスチック板、樹脂塗装面等の表面の保護シートあるいは一時的な固定用シートとしての粘着シートとして広く使用することができる。

【0050】

【実施例】以下、実施例を挙げて本発明を更に具体的に説明する。尚、実施例中「%」、「部」とあるのは、特に断りのない限り重量基準を表す。

【0051】以下の要領でポリイソシアネート系誘導体[A]を製造した。

・ポリイソシアネート系誘導体[A-1]

温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、イソホロンジイソシアネート132g(0.59モル)、水添ポリブタジエンポリオール(重量平均分子量2477、ヨウ素価21、水酸基価45.3mgKOH/g)490g(0.20モル)及び水添ポリブタジエンポリオール(重量平均分子量1740、ヨウ素価21、水酸基価64.5mgKOH/g)344g(0.20モル)を仕込み、90°Cで反応させ、残存イソシアネート基が1.7%となった時点で、温度を60°Cに下げ、4-ヒドロキシブチルアクリ

リレート 28.5 g (0.20モル) を加え反応させ、残存イソシアネート基が 0.8% となった時点で、メタノール 6.5 g (0.2モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A-1] [ガラス転移温度 -30°C、重量平均分子量 14,000] を得た。

【0052】・ポリイソシアネート系誘導体 [A-2]
温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、イソホロンジイソシアネート 154.2 g (0.69モル)、水添ポリブタジエンポリオール (重量平均分子量 1740、ヨウ素価 21、水酸基価 64.5 mg KOH/g) 804.5 g (0.46モル) を仕込み、90°Cで反応させ、残存イソシアネート基が 2.0% となった時点で、温度を 60°C に下げ、2-ヒドロキシエチルアクリレート 26.9 g (0.23モル) を加え反応させ、残存イソシアネート基が 1.0% となった時点で、イソプロピルアルコール 14.2 g (0.24モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A-2] [ガラス転移温度 -32°C、重量平均分子量 13,600] を得た。

【0053】・ポリイソシアネート系誘導体 [A-3]
温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、イソホロンジイソシアネート 128.1 g (0.58モル)、ポリエステルポリオール (アデカニューエース V14-90 : 平均分子量 1958、水酸基価 57.3 mg KOH/g) 846.4 g (0.43モル) を仕込み、90°Cで反応させ、残存イソシアネート基が 1.2% となった時点で、温度を 60°C に下げ、2-ヒドロキシエチルアクリレート 16.7 g (0.14モル) を加え反応させ、残存イソシアネート基が 0.6% となった時点で、イソプロピルアルコール 8.8 g (0.15モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A-2] [ガラス転移温度 -35°C、重量平均分子量 18,000] を得た。

【0054】・ポリイソシアネート系誘導体 [A-4]
温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、ヘキサメチレンジイソシアネート 113.9 g (0.61モル)、水添ポリブタジエンポリオール (重量平均分子量 2477、ヨウ素価 21、水酸基価 45.3 mg KOH/g) 499.6 g (0.20モル) 及び水添ポリブタジエンポリオール (重量平均分子量 1740、ヨウ素価 21、水酸基価 64.5 mg KOH/g) 350.9 g (0.20モル) を仕込み、90°Cで反応させ、残存イソシアネート基が 1.7% となった時点で、温度を 60°C に下げ、4-ヒ

ドロキシブチルアクリレート 29.0 g (0.20モル) を加え反応させ、残存イソシアネート基が 0.8% となった時点で、メタノール 6.6 g (0.21モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A-4] [ガラス転移温度 -18°C、重量平均分子量 13,500] を得た。

【0055】・ポリイソシアネート系誘導体 [A'-1]
1】

温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、イソホロンジイソシアネート 100.0 g (0.45モル)、水添ポリブタジエンポリオール (平均分子量 2343、ヨウ素価 21、水酸基価 47.9 mg KOH/g) 359 g (0.15モル) 及び水添ポリブタジエンポリオール (平均分子量 1740、ヨウ素価 21、水酸基価 64.5 mg KOH/g) 266.6 g (0.15モル) を仕込み、90°Cで反応させ、残存イソシアネート基が 1.4% となった時点で、温度を 60°C に下げ、4-ヒドロキシブチルアクリレート 43.5 g (0.3モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A'-1] [ガラス転移温度 -30°C、重量平均分子量 14,000] を得た。

【0056】・ポリイソシアネート系誘導体 [A'-2]
2】

温度計、攪拌機、水冷コンデンサー、窒素ガス吹き込み口を備えた4つ口フラスコに、イソホロンジイソシアネート 152 g (0.69モル)、ポリエステルポリオール (アデカニューエース V14-90 : 平均分子量 1958、水酸基価 57.3 mg KOH/g) 795 g (0.46モル) を仕込み、90°Cで反応させ、残存イソシアネート基が 2.0% となった時点で、温度を 60°C に下げ、2-ヒドロキシエチルアクリレート 53 g (0.46モル) を加え反応させ、残存イソシアネート基が 0.3% となった時点で反応を終了し、ポリイソシアネート系誘導体 [A'-2] [ガラス転移温度 -20°C、重量平均分子量 13,000] を得た。

【0057】また、エチレン性不飽和単量体 [B] としては、下記を用いた。

[B-1] : イソデシルアクリレート

[B-2] : シクロヘキシリルアクリレート

[B-3] : フェノキシエチルアクリレート

[B-4] : トリプロピレングリコールジアクリレート

[B-5] : 1,9-ノナンジオールジアクリレート

【0058】実施例 1~11、比較例 1~3

上記のポリイソシアネート系誘導体 [A]、エチレン性不飽和単量体 [B] を表 1 に示す如き配合量で混合し、更に光重合開始剤 (チバ・スペシャルティ・ケミカルズ社製、「ダロキュア 1173」) 4 部加えて、紫外線

硬化型粘着剤組成物を得た。

【表1】

【0059】

	ポリイソシアネート系誘導体【A】		イソブチレン系不飽和單量体【B】	
	種類	含有量(部)	種類	含有量(部)
実施例1	A-1	70	B-1	30
" 2	A-2	70	B-1	30
" 3	A-3	80	B-3	20
" 4	A-4	70	B-1	30
" 5	A-1	80	B-2	20
" 6	A-2	70	B-2	30
" 7	A-3	70	B-3/B-4	25/5
" 8	A-4	70	B-2	30
" 9	A-1	80	B-5	20
" 10	A-1	80	B-4	20
" 11	A-1	80	B-1/B-4	15/5
比較例1	A'-1	70	B-1	30
" 2	A'-2	70	B-4	30
" 3	イソブチレン系粘着剤 100部			

【0060】次いで、未処理ポリエチレンテレフタレート(PET)フィルム(厚さ50μ)に、得られた紫外線硬化型粘着剤組成物を膜厚25μとなるようにアブリケーターにて塗布し、卓上UV照射装置(岩崎電気社製、「コンベア式卓上照射装置」)にて80W/cm²(高圧水銀ランプ)×13cmH×1.5m/min×3Pass(積算3000mJ/cm²)の条件下で紫外線照射して硬化させ粘着剤シートを得た。

【0061】かかる粘着剤シートについて、以下の評価をした。結果を表2に示す。

(粘着性)SUS研磨板に上記粘着剤シートを貼り付け2kgローラーにて2往復、30分後の180度剥離試験(g/25cm)を行った。

【0062】(保持力)SUS研磨板に上記粘着剤シートを貼り付け面積が25mm×25mmになるように貼着し、40℃、65%RHの条件下にて1kgの荷重をかけて、JISZ0237に準拠して24時間後の保持力(ズレmm)を測定した。

【0063】(耐候性)粘着性測定に使用したシートについて、サンシャインウエザーメーター照射1000時間後の外観を以下の基準で、また、粘着性(g/25mm)を前記同様にして評価した。

○: 色調の変化がほとんど無い

△: 若干黄色味を帯びている
×: 著しく変色している

【0064】

【表2】

	粘着性 (g/25mm)	保持力 (J/mm)	耐候性	
			外観	粘着性(g/25mm)
実施例 1	1500	0.00	○	1480
" 2	1550	0.00	○	1500
" 3	1500	0.00	△	1000
" 4	1500	0.00	○	1480
" 5	1450	0.00	○	1410
" 6	1500	0.00	○	1450
" 7	1550	0.00	△	1000
" 8	1500	0.00	○	1500
" 9	1600	0.00	○	1600
" 10	1350	0.00	○	1350
" 11	1600	0.00	○	1550
比較例 1	1350	0.05	○	1300
" 2	900	0.50	△	600
" 3	900	0.05	×	30>

【0065】

【発明の効果】本発明の活性エネルギー硬化型粘着剤組成物は、ポリオール(a1)とポリイソシアネート(a2)との反応物であるイソシアネート基含有化合物[a]中のイソシアネート基が、水酸基含有(メタ)アクリレート(a3)の水酸基及び、飽和アルコール(a4)の水酸基と、それぞれウレタン結合を形成してなる

ポリイソシアネート系誘導体[A]、及びエチレン性不飽和単量体[B]を含有してなるため、基材との接着性と耐候性のバランスに優れており、紙、プラスチック板、金属、ガラス等の各種基材からなる物品の保護フィルム用途や自動車ボディ用の保護フィルム用途、或いは仮接着用の粘着シートに用いる粘着剤として有用な活性エネルギー線硬化型粘着剤組成物である。

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CC06 CC08 CD09
4J034 CA02 CA03 CA04 CA05 CA22
CA31 CB01 CB03 CB04 CB05
CB07 CB08 CC02 CC03 CC08
CC12 CC23 CC26 CC37 CC45
CC52 CC61 CC62 CC65 DA01
DB01 DB03 DB04 DB07 DF01
DF12 DF16 DF20 DF22 DF29
DG03 DG04 DG06 DG08 DG10
DG12 DH02 DH06 DP12 FA01
FB01 FC01 FD01 FE02 GA02
GA06 GA23 GA33 GA55 HA01
HA07 HB08 HC03 HC12 HC17
HC22 HC45 HC46 HC52 HC54
HC61 HC64 HC67 HC71 HC73
JA21 JA42 KA01 KB02 KC17
KD02 KE02 LA13 LA33 RA08
4J040 EF351 EF352 FA131 FA132
FA291 FA292 GA01 HB18
HC16 HD06 HD19 HD21 JA02
JB07 KA13 LA06 LA07 MA02
MA05 MA09 MA10 NA22 PA20
PA32
4J100 AL03Q AL04Q AL05Q AL08P
AL08Q AL09Q AL10Q AL62Q
AL63Q AL66P AL66Q AL67P
AL67Q AL75Q AR28Q BA02P
BA02Q BA03Q BA04Q BA08P
BA08Q BA15P BA15Q BA16P
BA16Q BA21P BA38P BA39P
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(54) ACTIVE-ENERGY-RAY-CURABLE PRESSURE-SENSITIVE ADHESIVE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a pressure-sensitive adhesion composition which is curable by active energy rays such as ultraviolet rays, especially a pressure-sensitive adhesive composition which is useful for protective films for articles made of various substrates such as paper, plastic boards, metals, and glass, for protective films for automotive bodies, and for pressure-sensitive adhesive sheet for temporary bonding.

SOLUTION: This pressure-sensitive adhesive composition contains a polyisocyanate derivative [A] and an ethylenically unsaturated monomer [B]. The polyisocyanate derivative [A] is prepared by reacting isocyanate groups of an isocyanate-group-containing compound [a] prepared by the reaction of a polyol (a1) with a polyisocyanate (a2) with the hydroxyl group of a hydroxyl- group-containing (meth)acrylate (a3) and the hydroxyl group of a saturated alcohol (a4) so as to form urethane bonds.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the protection film application of the goods which consist of various base materials, such as a binder constituent which hardens with activity energy lines, such as ultraviolet rays, and discovers an adhesion function especially paper, a plastic sheet, a metal, and glass, the protection film application for the automobile bodies, or an activity energy-line hardening mold binder constituent useful to the pressure sensitive adhesive sheet for temporary adhesion.

[0002]

[Description of the Prior Art] In recent years, as a binder used for protection films which consist of various base materials, such as paper, a plastic sheet, a metal, and glass, such as goods and the automobile body, it excels in adhesion physical properties, and also weatherability is needed so that it can apply to storage on the outdoors etc. Although acrylic resin and rubber system resin are conventionally used abundantly as this binder, there are merits and demerits in respect of balance with adhesion with a base material, or weatherability, and the improvement is required. Moreover, since conventional acrylic resin and rubber system resin are usually the thing of a solvent mold, they have the room of correspondence also from the point of an environmental problem.

[0003] On the other hand, examination of the binder of an activity energy-line hardening mold or adhesives is made from a predominance that hardening is completed very much by the exposure of short-time ultraviolet rays etc. For example, in JP,6-184498,A, the hardening mold adhesives constituent which consists of at least one sort chosen from the group which consists of an acrylic acid (meta) and carboxyl content (meta) acrylate, and polyurethane poly (meta) acrylate is indicated. It is indicated that the bond strength to a film is demonstrated and this adhesives constituent is used as adhesives for a lamination by carrying out electron ray hardening.

[0004] Moreover, in JP,11-189762,A, it is indicated that the resin constituent which consists of urethane acrylate which consists of polyester polyol, poly isocyanate, and mono-hydroxyalkyl acrylate, and a reactant diluent is used as a resin constituent for pressure sensitive adhesive sheet base materials. Furthermore, in JP,4-183770,A, the radiation-curing mold binder constituent which comes to contain the urethane (meta) acrylate oligomer which acrylate is made to react to the hydroxyl group in the reactant of hydrogenation polybutadiene polyol and the poly isocyanate, and is obtained, and monofunctional (meta) acrylate is indicated.

[0005]

[Problem(s) to be Solved by the Invention] Then, although this invention person etc. inquired that the resin constituent of the activity energy-line hardening mold known until now also including the above-mentioned official report indication technique should be applied to the above-mentioned binder for protection films, there is nothing that the balance of an adhesive property with a base material and weatherability was able to take with the sufficient forge fire, and the development is just going to desire. In this invention, it excels in the balance of an adhesive property with a base material, and weatherability under such a background, and aims at offering an activity energy-line hardening mold

binder constituent useful as a binder used for various protection films.

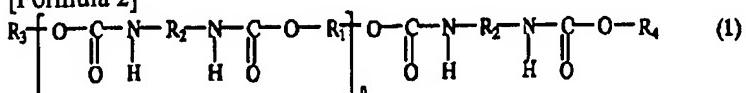
[0006]

[Means for Solving the Problem] As a result of repeating research wholeheartedly in view of this situation, however, the isocyanate radical in the isocyanate radical content compound [a] which is a reactant of polyol (a1) and the poly isocyanate (a2) this invention person etc. The hydroxyl group of hydroxyl-group content (meta) acrylate (a3), and the hydroxyl group of saturated alcohol (a4), The activity energy-line hardening mold binder constituent which comes to contain the poly isocyanate system derivative [A] which comes to form a urethane bond, respectively, and an ethylene claim partial saturation monomer [B] completed a header and this invention for agreeing for the above-mentioned purpose.

[0007] As for the poly isocyanate system derivative [A], in especially this invention, it is desirable that it is the structure shown at the following general formula (1) in respect of the high adhesive property of the hardening coat by activity energy-line exposure.

[0008]

[Formula 2]



Here, for R1, as for the both-ends urethane bond residue of the poly isocyanate (a2), and R3, the both-ends urethane bond residue of polyol (a1) and R2 are [the urethane bond residue of hydroxyl-group content (meta) acrylate (a3) and R4] the urethane bond residue of saturated alcohol (a4), and n is one or more integers.

[0009] Moreover, in this invention, when polyol (a1) is hydrogenation polybutadiene polyol and an ethylenic unsaturated monomer [B] is with a carbon numbers of six or more aliphatic series or alicycle group alkyl (meta) acrylate, the effectiveness of this invention is demonstrated notably.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The isocyanate radical in the isocyanate radical content compound [a] which is a reactant of polyol (a1) and the poly isocyanate (a2) explains below the poly isocyanate system derivative [A] used by this invention about the hydroxyl group of hydroxyl-group content (meta) acrylate (a3) and the hydroxyl group of saturated alcohol (a4), and each component from which it is the poly isocyanate system derivative which comes to form a urethane bond, respectively, and this poly isocyanate system derivative [A] is constituted.

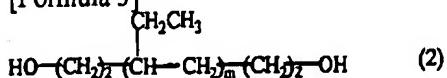
[0011] It is not limited especially as polyol (a1). For example, ethylene glycol, A diethylene glycol, triethylene glycol, tetraethylene glycol, A polyethylene glycol, propylene glycol, dipropylene glycol, A polypropylene glycol, a butylene glycol, 1,4-butanediol, A polybutylene glycol, 1,6-hexanediol, neopentyl glycol, Cyclohexane dimethanol, hydrogenation bisphenol A, the poly caprolactone, Trimethylolethane, trimethylol propane, poly trimethylol propane, Pentaerythritol, the poly pentaerythritol, a sorbitol, A mannitol, arabitol, xylitol, galactitol, a glycerol, Polyhydric alcohol, such as polyglycerin, a polytetramethylene glycol, and hydrogenation polybutadiene polyol, The polyether polyol which has the block of polyethylene oxide, polypropylene oxide, and ethyleneoxide / propylene oxide, or at least one sort of structures of random copolymerization, This polyhydric alcohol or polyether polyol and a maleic anhydride, a maleic acid, The polyester polyol which is a condensate with polybasic acid, such as boletic acid, itaconic acid anhydride, an itaconic acid, an adipic acid, and isophthalic acid, Caprolactone denaturation polyols, such as caprolactone denaturation polytetramethylene polyol, polyolefine system polyol, etc. are mentioned. Further 2 and 2-screw (hydroxymethyl) butanoic acid, a tartaric acid, 2, 4-dihydroxybenzoic acid, 3, 5-dihydroxybenzoic acid, 2, and 2-screw (hydroxymethyl) propionic acid, 2 and 2-screw (hydroxyethyl) propionic-acid, 2, and 2-screw (hydroxypropyl) propionic acid, Dihydroxy methylacetic acid, screw (4-hydroxyphenyl) acetic-acid, 4, and 4-screw (4-hydroxyphenyl) pentanoic acid, carboxyl group content polyols, such as a homogentisic acid, sulfonic groups, such as 1,4-butanediol sulfonic-acid sodium, or sulfonate radical

content polyol, etc. is mentioned -- having -- one sort -- or two or more sorts are used together and it is used. Also in the above-mentioned polyol (a1), especially hydrogenation polybutadiene polyol is preferably used weatherability and in respect of a water resisting property.

[0012] that this hydrogenation polybutadiene polyol is indicated to be by the following general formula (2) -- it is -- the molecular weight -- 300-6000 -- the thing of 500-3000 is preferably useful. moreover, the iodine number -- 0-50 -- it is 0-20 preferably and 30 - 250 mgKOH/g is preferably suitable for a hydroxyl value 15 to 400 mgKOH/g.

[0013]

[Formula 3]



Here, m is the integer of 3-110.

[0014] Especially as poly-isocyanate (a2), for example, without being limited An aromatic series system, The poly isocyanates, such as an aliphatic series system and an alicyclic system, are mentioned. Especially Tolylen diisocyanate, Diphenylmethane diisocyanate, hydrogenation-ized diphenylmethane diisocyanate, Denaturation diphenylmethane diisocyanate, hydrogenation-ized xylylene diisocyanate, Xylylene diisocyanate, hexamethylene di-isocyanate, trimethyl hexamethylene di-isocyanate, Tetramethyl xylylene diisocyanate, isophorone diisocyanate, Diisocyanate, such as norbornene diisocyanate, 1, and 3-screw (isocyanato methyl) cyclohexane, or these trimers, view let mold poly isocyanate, etc. are used suitably. As for the molecular weight of this poly isocyanate compound (a2), 150-700 are desirable from a reactant point with a hydroxyl group.

[0015] As hydroxyl-group content (meta) acrylate (a3) For example, without being limited especially 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, 2-hydroxyethyl acryloyl phosphate, 4-butyl hydroxy (meta) acrylate, 2-(meta) AKURIRO yloxy ethyl-2-hydroxypropyl phthalate, GURISERINJI (meta) acrylate, 2-hydroxy-3-AKURIRO yloxy propyl (meta) acrylate, Caprolactone denaturation 2-hydroxyethyl (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, dipentaerythritol PENTA (meta) acrylate, caprolactone denaturation 2-hydroxyethyl (meta) acrylate, etc. are mentioned. The hydroxyl-group content (meta) acrylate of 2-20 has the useful carbon number of an alkyl group in respect of adhesiveness and weatherability also in these.

[0016] Especially as saturated alcohol (a4), without being limited for example, alkyl monoalcohol (a methanol, ethanol, and n-propyl alcohol --) Isopropyl alcohol, a hexanol, decanol, lauryl alcohol, To stearyl alcohol and BE, the alcohol of carbon 1-22, such as nil alcohol, Ethylene glycol monoalkyl ether, diethylene-glycol monoalkyl ether, Propylene glycol monoalkyl ether, polypropylene-glycol monoalkyl ether, etc. are mentioned, and alkyl monoalcohol especially a methanol, ethanol, n-propyl alcohol, isopropyl alcohol, etc. are suitable especially.

[0017] The poly isocyanate system derivative [A] used by this invention Polyol (a1) and the poly isocyanate (a2) are made to react from the stability of reaction control, and a viewpoint of compaction of production time. After obtaining an isocyanate radical content compound [a], subsequently the isocyanate radical in this isocyanate radical content compound [a] The hydroxyl group of hydroxyl-group content (meta) acrylate (a3), and the hydroxyl group of saturated alcohol (a4), It is obtained by forming a urethane bond, respectively.

[0018] for example, in the case where an isocyanate radical content compound [a] has two isocyanate radicals One isocyanate radical forms the hydroxyl group and urethane bond of hydroxyl-group content (meta) acrylate (a3). The one remaining isocyanate radicals serve as the poly isocyanate system derivative [A] in which the hydroxyl group and urethane bond of saturated alcohol (a4) were formed. In the case where an isocyanate radical content compound [a] has three isocyanate radicals One isocyanate radical forms the hydroxyl group and urethane bond of hydroxyl-group content (meta) acrylate (a3) (or saturated alcohol (a4)). The two remaining isocyanate radicals serve as the poly isocyanate system derivative [A] in which the hydroxyl group and urethane bond of saturated alcohol (a4) (or hydroxyl-group content (meta) acrylate (a3)) were formed.

[0019] In performing the reaction which forms the above-mentioned urethane bond it limits especially -- not having -- (**) -- the approach of making hydroxyl-group content (meta) acrylate (a3) and saturated alcohol (a4) teaching and reacting to a package into an isocyanate radical content compound [a] -- (**), after making an isocyanate radical content compound [a] and hydroxyl-group content (meta) acrylate (a3) react Although approach ** to which hydroxyl-group content (meta) acrylate (a3) is made to react is mentioned after making the approach and isocyanate (Ha) radical content compound [a] to which saturated alcohol (a4) is made to react, and saturated alcohol (a4) react The approach of the stability of reaction control and the viewpoint of compaction of production time to (b) is desirable.

[0020] Moreover, in this reaction, it is also desirable to use catalysts, such as dibutyltin dilaurate, in order to promote a reaction, and especially reaction temperature has the still more desirable range of 40-70 degrees C 30-90 degrees C.

[0021] It is desirable that it is the structure shown by the above-mentioned general formula (1) also in the above-mentioned poly isocyanate system derivative [A] in this invention in respect of a high adhesive property, and it is desirable that n of the poly isocyanate system derivative shown especially at a general formula (1) is 1-15, and also 1-10.

[0022] In obtaining the poly isocyanate system derivative shown by this general formula (1), especially They are polyol (a1) and the poly isocyanate (a2) k:k +1 (mole ratio) (k is one or more integers.) After making it react by the reaction mole ratio and obtaining an isocyanate radical content compound [a], Hydroxyl-group content (meta) acrylate (a3) is made to react to this isocyanate radical content compound [a] by the reaction mole ratio of 1:1. furthermore, the method of making saturated alcohol (a4) react to the acquired resultant by the reaction mole ratio of 1:1 -- or The method of making saturated alcohol (a4) react to this isocyanate radical content compound [a] by the reaction mole ratio of 1:1, and making hydroxyl-group content (meta) acrylate (a3) react to the resultant acquired further by the reaction mole ratio of 1:1 is desirable. The former approach is preferably used from the stability of reaction control, and a viewpoint of compaction of production time especially.

[0023] Moreover, in manufacture of the above-mentioned poly isocyanate system derivative [A], when the poly isocyanate system derivative [A] obtained serves as hyperviscosity, the below-mentioned ethylenic unsaturated monomer [B] can be beforehand taught to a reaction can if needed, each component can be made to be able to react in an ethylenic unsaturated monomer [B], and the poly isocyanate system derivative [A] can also be manufactured.

[0024] Although the poly isocyanate system derivative [A] used by this invention in this way is obtained, it is desirable that the weight average molecular weight of the poly isocyanate system derivative [A] is 5,000-100,000 in this invention, and also it is desirable that it is 10,000-50,000. If adhesiveness becomes low and this weight average molecular weight exceeds 100,000, it worsens [coating nature] and is not desirable at less than 5,000.

[0025] In addition, the above-mentioned weight average molecular weight is weight average molecular weight by standard polystyrene molecular weight conversion, and is column:Shodex to high performance chromatography (the Showa Denko K.K. make, "ShodexGPC system-11 mold"). GPC It is measured by using 3 serials of KF-806L (exclusion-limit molecular weight: 2x10⁷, separation range:100-2x10⁷, theoretical plate number:10,000 step/a book, a bulking agent quality-of-the-material:styrene-divinylbenzene copolymer, bulking agent particle-size:10micrometer).

[0026] moreover, glass-transition-temperature [TMA (heat mechanical analysis) of the poly isocyanate system derivative [A] -- as measurement], 0 degree C or less is desirable by law, and -20 degrees C or less are still more desirable. When 0 degree C is exceeded, hardening contraction is large, and adhesiveness becomes low and is not desirable. furthermore -- this invention -- the ethylene nature partial saturation in poly isocyanate system [derivative A] 1 molecule -- it is desirable that the base is 1-3 pieces, and if three pieces are exceeded, the adhesive property of the hardening coat by activity energy-line exposure will fall, and it is not desirable.

[0027] Especially as an ethylenic unsaturated monomer [B] used by this invention, it is not limited, but monofunctional (meta) acrylate, 2 organic-functions (meta) acrylate, the acrylate (meta) of three or more organic functions, etc. are mentioned, monofunctional (meta) acrylate is especially effective from an

adhesive point especially, and with a carbon numbers of six or more aliphatic series or alicycle group alkyl (meta) acrylate is desirable.

[0028] As with a carbon numbers of six or more aliphatic series or alicycle group alkyl (meta) acrylate For example, hexyl (meta) acrylate, heptyl (meta) acrylate, Octyl (meta) acrylate, nonyl (meta) acrylate, DESHIRU (meta) acrylate, Isodecyl (meta) acrylate, dodecyl (meta) acrylate, Stearyl (meta) acrylate, lauryl (meta) acrylate, Cyclohexyl (meta) acrylate, isobornyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, tricyclo deca nil (meta) acrylate, etc. are mentioned, and isodecyl (meta) acrylate, lauryl (meta) acrylate, and cyclohexyl (meta) acrylate are used suitably especially.

[0029] As monofunctional (meta) acrylate other than with a carbon numbers of six or more aliphatic series or alicycle group alkyl (meta) acrylate For example, methyl (meta) acrylate, ethyl (meta) acrylate, Phenoxy ethyl (meta) acrylate, glycerol monochrome (meta) acrylate, Glycidyl (meta) acrylate, JISHIKURO pentenyl (meta) acrylate, n-butyl (meta) acrylate, benzyl (meta) acrylate, Phenol ethyleneoxide denaturation ($n=2$) (meta) acrylate, Nonyl phenol propylene oxide denaturation ($n=2.5$) (meta) acrylate, 2-(meta) acryloyloxy ethyl acid phosphate, furfuryl (meta) acrylate, Carbitol (meta) acrylate, benzyl (meta) acrylate, Butoxy ethyl (meta) acrylate, allyl compound (meta) acrylate, 2-hydroxyethyl (meta) acrylate, 2-hydroxypropyl (meta) acrylate, 2-hydroxy butyl (meta) acrylate, 2-phenoxy-2-hydroxypropyl (meta) acrylate, 2-hydroxy-3-phenoxy propyl (meta) acrylate, 3-chloro-2-hydroxypropyl (meta) acrylate, etc. are mentioned. Also in these, the monofunctional (meta) acrylate which does not contain a hydroxyl group is desirable, and this acrylate whose molecular weight is 100 to about 300 is still more desirable.

[0030] As 2 organic-functions (meta) acrylate, for example Ethylene GURIKORUJI (meta) acrylate, Diethylene GURIKORUJI (meta) acrylate, tetra-ethylene GURIKORUJI (meta) acrylate, Polyethylene GURIKORUJI (meta) acrylate, propylene GURIKORUJI (meta) acrylate, Zypor pyrene GURIKORUJI (meta) acrylate, polypropylene GURIKORUJI (meta) acrylate, Butylene GURIKORUJI (meta) acrylate, neopentyl GURIKORUJI (meta) acrylate, Ethyleneoxide denaturation bisphenol A mold di(meth) acrylate, Propylene oxide denaturation bisphenol A mold di(meth)acrylate, 1, 6-hexane JIORUJI (meta) acrylate, GURISERINJI (meta) acrylate, Pen TAERISURITORUJI (meta) acrylate, etyleneglycol diglycidylether di(meta)acrylate, Diethylene-glycol diglycidyl ETERUJI (meta) acrylate, phthalic-acid diglycidyl S TERUJI (meta) acrylate, hydroxy pivalate denaturation neopentyl GURIKORUJI (meta) acrylate, etc. are mentioned.

[0031] As acrylate (meta) of three or more organic functions, TORIMECHI roll pro pantry (meta) acrylate, pen TAERISURITORUTORI (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, dipentaerythritol PENTA (meta) acrylate, dipentaerythritol hexa (meta) acrylate, Tori (meta) acryloyl oxyethoxy trimethylol propane, glycerol poly glycidyl ether poly (meta) acrylate, etc. are mentioned, for example.

[0032] Moreover, the Michael addition product of an acrylic acid or 2-acryloyloxyethyl dicarboxylic acid monoester is also mentioned besides the above as an ethylenic unsaturated monomer [B].

[0033] As a Michael addition product of an acrylic acid, also while an acrylic-acid dimer [following the (3) type], a methacrylic-acid dimer, an acrylic-acid trimer [following the (4) type], a methacrylic-acid trimer, an acrylic-acid tetramer [following the (5) type], a methacrylic-acid tetramer, etc. are mentioned, an acrylic-acid dimer is desirable.

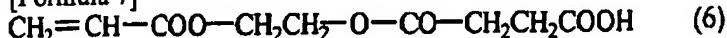
[0034]



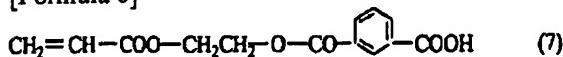
[0035] With moreover, 2-acryloyloxyethyl dicarboxylic acid monoester It is a carboxylic acid with a specific substituent. For example, 2-acryloyloxyethyl succinic-acid monoester [following the (6) type], 2-methacryloiloxy-ethyl succinic-acid monoester, 2-acryloyloxyethyl phthalic-acid monoester [following the (7) type], 2-methacryloiloxy-ethyl phthalic-acid monoester, 2-acryloyloxyethylhexahydrophthalic acid monoester [following the (8) type], 2-methacryloyloxyethylhexahydrophthalic acid monoester etc. is mentioned and it is 2-acryloyloxyethylhexahydrophthalic acid monoester preferably. Furthermore, in addition to this, oligoester acrylate [following the (9) type] can be mentioned.

[0036]

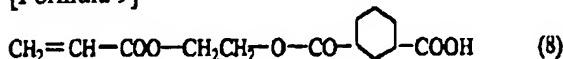
[Formula 7]



[Formula 8]



[Formula 9]



[Formula 10]



[0037] The above-mentioned ethylenic unsaturated monomer [B] may be used independently, or two or more sorts may be used together and it may be used.

[0038] moreover, in this invention, [A]: [B] is 10:90-95:5 (weight ratio) about the content of the above-mentioned poly isocyanate system derivative [A] and an ethylenic unsaturated monomer [B] -- desirable -- further -- it is desirable that it is 50:50-80:20 (weight ratio). It arises [adhesion worsens / the content of the poly isocyanate system derivative [A] / under in the above-mentioned range, if the above-mentioned range is crossed on the other hand, coating nature will worsen, and / a problem] practically and is not desirable.

[0039] It is desirable to use a photopolymerization initiator [C] together further in this invention. As this photopolymerization initiator [C] It will not be limited especially if a radical is generated according to an operation of light. Specifically 4-phenoxy dichloro acetophenone, a 4-t-butyl-dichloro acetophenone, A diethoxy acetophenone, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON, 1-(4-isopropanal pyrene phenyl)-2-hydroxy-isobutane-1-ON, 1-(4-dodecyl phenyl)-2-hydroxy-isobutane-1-ON, 4 -(2-hydroxy ethoxy)- Phenyl (2-hydroxy-2-propyl) ketone, 1-hydroxy cyclohexyl phenyl ketone, the 2-methyl-1-[4-(methylthio) phenyl]-2-morpholino propane -1, a benzoin, Benzoin methyl ether, benzoin ethyl ether, benzoin iso-propyl ether, Benzoin isobutyl ether, benzyl dimethyl ketal, a benzophenone, Benzoylbenzoic acid, methyl o-benzoylbenzoate, 4-phenylbenzo phenon, A hydroxy benzophenone, 4-benzoyl-4'-methyl diphenyl sulfide, 3 and 3'-dimethyl-4-methoxybenzophenone, thioxanthone, 2-KURORU thioxanthone, 2-methylthioxanthone, 2, 4-dimethylthioxanthone, Isoprophylthioxanthone, a camphor quinone, dibenzosulfone, 2-ethylanthraquinone, 4', 4"-diethyl isophthalophenone, A 3, 3', 4, and 4'-tetrapod (tert-butyl peroxide carbonyl) benzophenone, alpha-ASHIROKI SIMM ester, acyl phosphine oxide, methylphenylglyoxylate, Benzyl, 9, 10-phenanthrene quinone, a 4-(2-hydroxy ethoxy) phenyl-(2-hydroxy-2-propyl) ketone, etc. are mentioned. Especially Benzyl dimethyl ketal, 1-hydroxy cyclohexyl phenyl ketone, Benzoyl isopropyl ether, 4 -(2-hydroxy ethoxy)- A phenyl (2-hydroxy-2-propyl) ketone, 2-hydroxy - 2-methyl-1-phenyl propane-1-ON is used suitably.

[0040] About the loadings of this photopolymerization initiator [C], it is desirable that it is 1 - 10 weight section to a total of 100 weight sections of the poly isocyanate system derivative [A] and an ethylenic unsaturated monomer [B], and it is 2 - 5 weight section more preferably. Hardenability improves and is useless, even if these loadings become [the cure rate in the case of ultraviolet curing] very slow in

under 1 weight section and it exceeds 10 weight sections.

[0041] Furthermore, it is also possible to use together triethanolamine, tri-isopropanolamine, 4, and 4'-dimethylamino benzophenone (Michler's ketone), 4, and 4'-diethylamino benzophenone, 2-dimethylaminoethyl benzoic-acid, 4-dimethylamino ethyl benzoate, 4-dimethylamino benzoic-acid (n-butoxy) ethyl, 4-dimethylamino isoamyl benzoate, 4-dimethylamino benzoic-acid 2-ethylhexyl, 2, 4-diethyl thioxanthone, 2, and 4-diisopropyl thioxanthone etc. as an assistant of a photopolymerization initiator if needed.

[0042] Moreover, it is also possible to blend an anti-oxidant, a flame retarder, an antistatic agent, a bulking agent, a leveling agent, a stabilizer, a reinforcing agent, a flattening, etc. besides the above-mentioned poly isocyanate system derivative [A], an ethylenic unsaturated monomer [B], and a photopolymerization initiator [C]. Furthermore, an epoxy compound, a horse mackerel lysine compound, a melamine compound, an isocyanate compound, a chelate compound, etc. can be used for the compound and concrete target which have the operation which causes bridge formation with heat as a cross linking agent.

[0043] Moreover, addition of rosin, a rosin ester compound, a pinene system polymer, hydrogenation petroleum resin, hydrocarbon resin, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, 3-methylpentane-1,3,5-triol, etc. does not interfere as an adhesion grant nature compound, either.

[0044] Moreover, it can blend suitably, ethyl acetate, toluene, a xylene, a methanol, ethanol, a butanol, an acetone, methyl isobutyl ketone, a methyl ethyl ketone, cellosolves, diacetone alcohol, etc. are mentioned as this solvent, and a solvent can also be added about 1 to 50% of the weight to the total quantity of the poly isocyanate system derivative [A] and an ethylenic unsaturated monomer [B].

[0045] The binder constituent of this invention is usually applied to a base material sheet etc., practical use is presented with it as a pressure sensitive adhesive sheet, adhesive tape, etc. in many cases, it is hardened by activity energy-line exposure and adhesiveness is made to discover it after applying to a base material.

[0046] As a base material to apply, a polyvinyl chloride, polybutene, polybutadiene, Polyurethane, an ethylene-vinylacetate copolymer, polyethylene terephthalate, Polyethylene, a PORIPIRO pyrene, ethylene propylene rubber, the poly methyl pentene, Bright films, such as polybutylene terephthalate, are mentioned. For the protection film application of the paint film of the automobile body, especially A polyethylene film, The polyethylene film with which a weathering agent and other additives were blended The surface-protection application of the concave convex in the back grinding process of a semi-conductor wafer, When expanded one in a dicing process uses for a required application The coloured film in which the transparency or activity energy-line transparency of the polyvinyl chloride which is excellent in flexibility and ductility, polyethylene, polypropylene, ethylene propylene rubber, an ethylene-vinylacetate copolymer, etc. is possible is used suitably.

[0047] As this activity energy line, although an electron ray besides electromagnetic waves, such as beams of light, such as far ultraviolet rays, ultraviolet rays, a near ultraviolet ray, and infrared radiation, an X-ray, and a gamma ray, a proton line, a neutron beam, etc. can be used, hardening according to the UV irradiation from a price etc. in the ease of carrying out of acquisition of a cure rate and irradiation equipment is advantageous. Moreover, it can also heat-treat at the temperature of about 80-200 degrees C following an activity energy-line exposure.

[0048] What is necessary is just to irradiate about two 100 - 3000 mJ/cm preferably about two 100 - 4000 mJ/cm as an approach of stiffening by UV irradiation using the high-pressure mercury lamp which emits the light of 150-450nm wavelength region, an ultrahigh pressure mercury lamp, a carbon arc lamp, a metal halide lamp, a xenon lamp, a chemical lamp, etc.

[0049] Since the activity energy-line hardening mold binder constituent of this invention has removability, it can be widely used as a pressure sensitive adhesive sheet as a surface protection sheet or surface temporary sheets for immobilization, such as a metal plate, a glass plate, a plastic sheet, and a resin painted surface.

[0050]

[Example] Hereafter, an example is given and this invention is explained still more concretely. In

addition, especially, it expresses weight criteria that it is with "%" and the "section" among an example, as long as there is no notice.

[0051] The poly isocyanate system derivative [A] was manufactured in the following ways.

- The poly isocyanate system derivative [A-1] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, isophorone diisocyanate 132g (0.59 mols), Hydrogenation polybutadiene polyol 490g (0.20 mols) and hydrogenation polybutadiene polyol (weight-average-molecular-weight 1740, iodine number 21, hydroxyl value 64.5 mgKOH/g) 344g (0.20 mols) are taught. (Weight average molecular weight 2477, the iodine number 21, hydroxyl value 45.3 mgKOH/g) When it is made to react at 90 degrees C and a residual isocyanate radical becomes 1.7% When lowered temperature to 60 degrees C, and add 4-hydroxy butyl acrylate 28.5g (0.20 mols), it is made to react and a residual isocyanate radical becomes 0.8% the time of adding methanol 6.5g (0.2 mols), making it react, and a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A-1 [the glass transition temperature of -30 degrees C and weight average molecular weight 14,000]] was obtained.

[0052] - The poly isocyanate system derivative [A-2] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, isophorone diisocyanate 154.2g (0.69 mols), When teach hydrogenation polybutadiene polyol (weight-average-molecular-weight 1740, iodine number 21, hydroxyl value 64.5 mgKOH/g) 804.5g (0.46 mols), it is made to react at 90 degrees C and a residual isocyanate radical becomes 2.0% When lowered temperature to 60 degrees C, and add 2-hydroxyethyl acrylate 26.9g (0.23 mols), it is made to react and a residual isocyanate radical becomes 1.0% the time of adding isopropyl alcohol 14.2g (0.24 mols), making it react, and a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A-2 [the glass transition temperature of -32 degrees C and weight average molecular weight 13,600]] was obtained.

[0053] - The poly isocyanate system derivative [A-3] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, isophorone diisocyanate 128.1g (0.58 mols), Polyester polyol (ADEKA new ace V14-90: average-molecular-weight 1958, hydroxyl value 57.3 mgKOH/g) 846.4g (0.43 mols) is taught. When it is made to react at 90 degrees C and a residual isocyanate radical becomes 1.2% When lowered temperature to 60 degrees C, and add 2-hydroxyethyl acrylate 16.7g (0.14 mols), it is made to react and a residual isocyanate radical becomes 0.6% the time of adding isopropyl alcohol 8.8g (0.15 mols), making it react, and a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A-2 [the glass transition temperature of -35 degrees C and weight average molecular weight 18,000]] was obtained.

[0054] - The poly isocyanate system derivative [A-4] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, hexamethylene di-isocyanate 113.9g (0.61 mols), Hydrogenation polybutadiene polyol 499.6g (0.20 mols) and hydrogenation polybutadiene polyol (weight-average-molecular-weight 1740, iodine number 21, hydroxyl value 64.5 mgKOH/g) 350.9g (0.20 mols) are taught. (Weight average molecular weight 2477, the iodine number 21, hydroxyl value 45.3 mgKOH/g) When it is made to react at 90 degrees C and a residual isocyanate radical becomes 1.7% When lowered temperature to 60 degrees C, and add 4-hydroxy butyl acrylate 29.0g (0.20 mols), it is made to react and a residual isocyanate radical becomes 0.8% the time of adding methanol 6.6g (0.21 mols), making it react, and a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A-4 [the glass transition temperature of -18 degrees C and weight average molecular weight 13,500]] was obtained.

[0055] - The poly isocyanate system derivative [A'-1] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, isophorone diisocyanate 100.0g (0.45 mols), Hydrogenation polybutadiene polyol 359g (0.15 mols) and hydrogenation polybutadiene polyol (average-molecular-weight 1740, iodine number 21, hydroxyl value 64.5 mgKOH/g) 266.6g (0.15 mols) are taught. (Average molecular weight 2343, the iodine number 21, hydroxyl value 47.9 mgKOH/g) When it is made to react at 90 degrees C and a residual isocyanate radical becomes 1.4% Lower temperature to 60 degrees C, and add 4-hydroxy butyl acrylate 43.5g (0.3

mols), and it is made to react. the time of a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A'-1 [the glass transition temperature of -30 degrees C and weight average molecular weight 14,000]] was obtained.

[0056] - The poly isocyanate system derivative [A'-2] thermometer, an agitator, a water cooled condenser, In 4 opening flask equipped with nitrogen gas entrainment opening, isophorone diisocyanate 152g (0.69 mols), Polyester polyol (ADEKA new ace V14-90: average-molecular-weight 1958, hydroxyl value 57.3 mgKOH/g) 795g (0.46 mols) is taught. When it is made to react at 90 degrees C and a residual isocyanate radical becomes 2.0% Lower temperature to 60 degrees C, and add 2-hydroxyethyl acrylate 53g (0.46 mols), and it is made to react. the time of a residual isocyanate radical becoming 0.3% -- a reaction -- ending -- the poly isocyanate system derivative -- [A'-2 [the glass transition temperature of -20 degrees C and weight average molecular weight 13,000]] was obtained.

[0057] Moreover, the following was used as an ethylenic unsaturated monomer [B].

[B-1]: Isodecyl acrylate [B-2]:cyclohexyl acrylate [B-3]:phenoxy ethyl acrylate [B-4] : tripropylene-glycol-diacrylate [B-5]:1, 9-nonane diol diacrylate [0058] It mixed with the *** loadings which show the poly isocyanate system derivative [A] of examples 1-11, the example 1 of a comparison - 3 above, and an ethylenic unsaturated monomer [B] in Table 1, and the photopolymerization initiator (Ciba Specialty Chemicals make, "DAROKYUA 1173") 4 section, in addition an ultraviolet curing mold binder constituent were obtained further.

[0059]

[Table 1]

	アリリシアート系誘導体 [A]		イソレ性不飽和單量体 [B]	
	種類	含有量 (部)	種類	含有量 (部)
実施例 1	A-1	70	B-1	30
" 2	A-2	70	B-1	30
" 3	A-3	80	B-3	20
" 4	A-4	70	B-1	30
" 5	A-1	80	B-2	20
" 6	A-2	70	B-2	30
" 7	A-3	70	B-3 / B-4	25 / 5
" 8	A-4	70	B-2	30
" 9	A-1	80	B-5	20
" 10	A-1	80	B-4	20
" 11	A-1	80	B-1 / B-4	15 / 5
比較例 1	A' - 1	70	B-1	30
" 2	A' - 2	70	B-4	30
" 3	イソブチレン系粘着剤 100部			

[0060] Subsequently, the obtained ultraviolet curing mold binder constituent was applied by the applicator so that it might become 25micro of thickness, with desk UV irradiation equipment (the Iwasaki Electric Co., Ltd. make, "conveyor type desk irradiation equipment"), UV irradiation is carried out to an unsettled polyethylene terephthalate (PET) film (50micro in thickness), it was stiffened under the conditions of 80 W/cm (high-pressure mercury lamp) x13cmHx1.5 m/minx3Pass (addition 3000 mJ/cm²), and the binder sheet was obtained.

[0061] The following evaluations were carried out about this binder sheet. A result is shown in Table 2. (Adhesiveness) The above-mentioned binder sheet was stuck on the SUS polish plate, and 2kg roller performed the 180-degree friction test (g/25cm) two round trips and 30 minutes after.

[0062] (Holding power) The holding power (gap mm) 24 hours after carrying out a semi-place to JISZ0237 was measured, having applied [stuck so that the above-mentioned binder sheet might be stuck on an SUS polish plate and area might be set to 25mmx25mm, and] the 1kg load under the conditions of 40 degrees C and 65%RH.

[0063] (Weatherability) the sheet used for adhesive measurement -- the appearance 1000 hours after a sunshine weather meter exposure -- the following criteria -- it is -- moreover, adhesiveness (g/25mm) -- said -- it evaluated similarly.

O : -- **: which does not almost have change of a color tone -- x: which wears the yellow taste a little --

[0064] discolored remarkably

[Table 2]

	粘着性 (g/25mm)	保持力 (X/mm)	耐候性	
			外観	粘着性(g/25mm)
実施例 1	1500	0.00	○	1480
" 2	1550	0.00	○	1500
" 3	1500	0.00	△	1000
" 4	1500	0.00	○	1480
" 5	1450	0.00	○	1410
" 6	1500	0.00	○	1450
" 7	1550	0.00	△	1000
" 8	1500	0.00	○	1500
" 9	1600	0.00	○	1600
" 10	1350	0.00	○	1350
" 11	1600	0.00	○	1550
比較例 1	1350	0.05	○	1300
" 2	900	0.50	△	600
" 3	900	0.05	x	30>

[0065]

[Effect of the Invention] The activity energy hardening mold binder constituent of this invention The isocyanate radical in the isocyanate radical content compound [a] which is a reactant of polyol (a1) and the poly isocyanate (a2) The hydroxyl group of hydroxyl-group content (meta) acrylate (a3), and the hydroxyl group of saturated alcohol (a4), Since it comes to contain the poly isocyanate system derivative [A] which comes to form a urethane bond, respectively, and an ethylenic unsaturated monomer [B], It excels in the balance of an adhesive property with a base material, and weatherability. Paper, a plastic sheet, They are the protection film application of the goods which consist of various base materials, such as a metal and glass, a protection film application for the automobile bodies, or an activity energy-line hardening mold binder constituent useful as a binder used for the pressure sensitive adhesive sheet for temporary adhesion.

[Translation done.]

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(54) SELF-ADHESIVE COMPOSITION AND SELF-ADHESIVE ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an acrylic self-adhesive compsn. excellent in heat resistance and adhesion to a substrate foam by compounding an acrylic copolymer obtd. mainly from an alkyl (meth)acrylate with a tackifying resin and an isocyanate- based crosslinker.

SOLUTION: An acrylic copolymer of 100 pts.wt. obtd. by the free-radical copolymn. of 59.5-98.99wt.% alkyl (meth)acrylate (X1) having a 2-18C alkyl group, 0.01-0.5wt.% hydroxylated vinyl monomer (X2) free-radical-copolymerizable with X1, 1-10wt.% polymerizable



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the adhesion workpiece using an acrylic binder constituent and it excellent in the adhesion to a foam base material, and thermal resistance.

[0002]

[Description of the Prior Art] As for adhesion workpieces, such as adhesive tape and a pressure sensitive adhesive sheet, what carried out the laminating of the binder constituent on the surface of the base material, and was used as a pressure sensitive adhesive double coated tape, foam adhesive tape, etc. is common, and they are broadly used for the application of building materials, home electronics, the shock absorbing material for automobiles, a crevice tape, etc.

[0003] Many solvent mold binder constituents which make acrylic resin a subject as such a binder constituent for adhesion workpieces at a point excellent in weatherability, endurance, thermal resistance, cold resistance, a water resisting property, etc. are used. In recent years, the more advanced thing also about many properties of the acrylic binder constituent used is required with application expansion of such an adhesion workpiece.

[0004] Since a base material is porosity, the adhesive tape which uses various rubber system foam as a base material is difficult for carrying out direct coating of the binder constituent solution to a foam base material, and after once carrying out coating of the binder constituent solution to a release paper etc. and drying, generally the manufacture approach which carries out a sticking-by-pressure imprint is performed to the foam base material. However, when this approach is used for a base material with large expansion ratio, such as urethane foam, the adhesion area by imprint runs short and there are troubles, like the adhesion to the foam base material of a binder constituent layer becomes low.

[0005] In the acrylic binder constituent which contains an acrylic polymer and a tackifier as a principal component in JP,3-281587,A Although it is indicated that the acrylic binder constituent with which a tackifier makes resin acid and polyhydric alcohol react, and is obtained and whose hydroxyl values of this resin acid ester it is resin acid ester and are 50-100 is excellent in many properties This acrylic binder constituent runs short of the adhesion area by imprint, when it is used for a base material with large expansion ratio, such as urethane foam, and the adhesion to a base material becomes low.

[0006] Although there was the approach of lowering the elastic modulus of a binder constituent desiccation coat by adding the low tackifier of a liquefied component or softening temperature simply to an acrylic binder constituent as an approach of solving the above-mentioned trouble, by this approach, there was a fault of the thermal resistance of a binder constituent falling.

[0007]

[Problem(s) to be Solved by the Invention] This invention aims at offering the acrylic binder constituent which was excellent in the adhesion to the base material of high expansion ratio, and was excellent in thermal resistance, and the adhesion workpiece using it in view of the above.

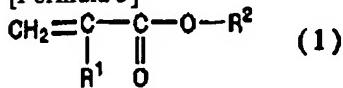
[0008]

[Means for Solving the Problem] A binder constituent (henceforth "this invention 1") according to claim

1 contains a hydroxyl group in 59.5 - 98.99 % of the weight (X-1) of acrylic-acid alkyl ester monomers whose carbon numbers of an alkyl group are 2-18 (meta), and a molecule, and is the above-mentioned (meta) acrylic-acid alkyl ester monomer (X-1), 0.01 - 0.5 % of the weight (X-2) of vinyl system monomers in which radical copolymerization is possible, and the following general formula (1);

[0009]

[Formula 3]



[0010] (R1 expresses hydrogen or a methyl group among a formula.) R2 Weight average molecular weight is 2000-50,000, and the non-polymerization nature polymer whose glass transition temperature is -30 degrees C or less is expressed. 1 - 10 % of the weight of polymerization nature polymers expressed, And the acrylic (copolymer A) 100 weight section obtained by carrying out radical copolymerization of the above-mentioned (meta) acrylic-acid alkyl ester monomer (X-1) and the 0 - 30 % of the weight (X-3) of the vinyl system monomers which can be copolymerized, softening temperature -- 120 - 145 -- degree C -- it is -- a tackifier -- (B) -- two - 30 -- weight -- the section -- a list -- an isocyanate cross-linking agent -- (C) -- 0.01 - five -- weight -- the section -- from -- becoming -- ethyl acetate -- receiving -- insoluble matter -- a rate -- 20 - 50 -- % of the weight -- it is -- things -- the description -- ** -- carrying out -- a thing -- it is .

[0011] A binder constituent (henceforth "this invention 2") according to claim 2 is characterized by becoming the acrylic copolymer 100 weight section according to claim 1, the rosin ester system tackifier (B-1) 2 which is 120-160 degrees C of softening temperatures - 20 weight sections, the liquefied tackifier (B-2) 0.1 - 5 weight sections, and a list from an isocyanate cross-linking agent 0.01 - 5 weight sections.

[0012] A binder constituent (henceforth "this invention 3") according to claim 3 Are a binder constituent according to claim 1 or 2, and an acrylic copolymer (A) makes an initiator the peroxide (Z) which has two or more peroxy association in a monad. The mixture of either the following monomer mixture (X) or monomer mixture (Y) is added, and the first step of polymerization is performed. Subsequently It is characterized by being obtained by adding the monomer mixture (X) which was not used for this by the first step of polymerization, or (Y), and performing the second step of polymerization.

[0013] 59.5 - 98.99 % of the weight (X-1) of acrylic-acid alkyl ester monomers whose carbon numbers of an alkyl group of monomer mixture (X) are 2-18 here (meta), A hydroxyl group is contained in a molecule. An acrylic-acid alkyl ester monomer (X-1) and 0.01 - 0.5 % of the weight (X-2) of vinyl system monomers in which radical copolymerization is possible, It consists of the above-mentioned (meta) acrylic-acid alkyl ester monomer (X-1) and 0 - 30 % of the weight (X-3) of vinyl system monomers in which radical copolymerization is possible.

[0014] Monomer mixture (Y) consists of 70 - 100 % of the weight (Y-1) of acrylic-acid alkyl ester monomers whose glass transition temperature when considering as a homopolymer is -30 degrees C or less (meta), and the above-mentioned (meta) acrylic-acid alkyl ester monomer (Y-1) and 0 - 30 % of the weight (Y-2) of vinyl system monomers in which radical copolymerization is possible.

[0015] A binder constituent according to claim 4 is a binder constituent according to claim 1 to 3, and weight ratio [of monomer mixture (X) and monomer mixture (Y)] (X)/(Y) is used by 70-99/30. [1-30]

[0016] An adhesion workpiece according to claim 5 is characterized by coming to carry out the laminating of at least one sort to other goods of a binder constituent according to claim 1 to 4.

[0017] This invention is explained in full detail below. It is not limited especially as an acrylic-acid (meta) alkyl ester monomer (X-1) which constitutes an acrylic copolymer (A), for example, an ethyl acrylate (meta), acrylic-acid (meta) n-butyl, 2-ethylhexyl acrylate (meta), acrylic-acid (meta) n-octyl, acrylic-acid (meta) iso octyl, acrylic-acid (meta) lauryl, etc. are mentioned. Acrylic-acid (meta) n-butyl, 2-ethylhexyl acrylate (meta), etc. are used suitably.

[0018] Moreover, it is not limited especially as a vinyl system monomer (X-2), for example, acrylic-acid (meta) 2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), acrylic-acid (meta) 2-hydroxy butyl, etc. are mentioned.

[0019] The polymerization nature polymer expressed with a general formula (1) is a macro monomer, has the acrylate (meta) radical of polymerization nature at one end, and is the polymer segment R2 of non-polymerization nature to the end of another side. It has.

[0020] Above R2 The non-polymerization nature polymer segment with which it is expressed is weight average molecular weight 2000-50,000, and glass transition temperature is -30 degrees C or less. If weight average molecular weight becomes small too much, it will become small too much to the elastic modulus of a hot binder constituent, and thermal resistance and creep resistance will fall. Moreover, since the reactivity of a polymerization nature polymer will fall if weight average molecular weight becomes large too much, it is limited to the above-mentioned range. It is 3000-20,000 preferably.

Furthermore, when glass transition temperature exceeds -30 degrees C, the elastic modulus of the binder constituent in ordinary temperature is large, and since the adhesion to a foam base material falls, it is limited to the above-mentioned range.

[0021] Non-polymerization nature polymer segment R2 As a suitable thing, Pori n-butyl acrylate, Pori 2-ethylhexyl acrylate, etc. are mentioned, for example.

[0022] It is not limited especially as the above-mentioned vinyl system monomer (X-3), for example, a methyl acrylate (meta), acrylic-acid (meta) benzyl, acrylic-acid (meta) cyclohexyl, acrylic-acid (meta) isobornyl, acrylamide (meta), acrylonitrile (meta), N-vinyl pyrrolidone, vinyl acetate, styrene, an acrylic acid (meta), a maleic anhydride, an itaconic acid, a crotonic acid, etc. are mentioned.

[0023] (Meta) Since cohesive force will decline and thermal resistance and creep resistance will worsen if a tuck falls that an acrylic-acid alkyl ester monomer (X-1) is less than 59.5 % of the weight and it exceeds 98.99 % of the weight, it is limited to the above-mentioned range. Since it becomes that a vinyl system monomer (X-2) is less than 0.01 % of the weight constructing a bridge inadequate, and thermal resistance and creep resistance fall, a bridge will be constructed too much if it exceeds 0.5 % of the weight, and a tuck and adhesion decline, it is limited to the above-mentioned range.

[0024] Since an elastic modulus [in / that a polymerization nature polymer is less than 1 % of the weight / ordinary temperature] is high, the adhesion to a foam base material falls, and thermal resistance will fall in order to make it fall greatly to a hot elastic modulus if it exceeds 10 % of the weight, it is limited to the above-mentioned range. Since a binder constituent will become hard and a tuck and adhesion will decline if a vinyl system monomer (X-3) exceeds 30 % of the weight, it is limited to the above-mentioned range.

[0025] this invention -- one -- a binder -- a constituent -- the above -- acrylic -- a copolymer -- (- A --) - - 100 -- weight -- the section -- softening temperature -- 120 - 145 -- degree C -- it is -- a tackifier -- (- B --) -- two - 30 -- weight -- the section -- and -- an isocyanate cross-linking agent -- (- C --) -- 0.01 - five -- weight -- the section -- from -- becoming .

[0026] The softening temperature of the above-mentioned tackifier (B) is 120-145 degrees C. Since the elastic modulus near the ordinary temperature of a binder constituent will become high and the adhesion to a foam base material will fall if the elastic modulus near the elevated temperature of a binder constituent is low, thermal resistance is bad in it being less than 120 degrees C and it exceeds 145 degrees C, it is limited to the above-mentioned range. It is 125-140 degrees C preferably.

[0027] Although it is not limited especially as a tackifier (B) but rosin system resin, terpene phenol system resin, petroleum resin, etc. are mentioned, rosin system resin is suitably used from the point of excelling in the balance of adhesion physical properties. For example, super ester A100 (the Arakawa chemical-industry company make, 100 degrees C of softening temperatures), super ester A115 (the Arakawa chemical-industry company make, 115 degrees C of softening temperatures), super ester A125 (the Arakawa chemical-industry company make, 125 degrees C of softening temperatures), the pen cel D125 (the Arakawa chemical-industry company make, 125 degrees C of softening temperatures), the pen cel D135 (the Arakawa chemical-industry company make, 135 degrees C of softening temperatures) the pen cel D160 (the Arakawa chemical-industry company make, 160 degrees C of softening

temperatures), etc. be mentioned These resin may be used independently and may use two or more kinds together. When using two or more kinds together, average softening temperature (formula: sigma (softening temperature x number of copies)/sigma number of copies) should just be in the above-mentioned range.

[0028] The loadings of a tackifier (B) are 2 - 30 weight section to the above-mentioned (copolymer A) 100 weight section. [acrylic] Since adhesion [as opposed to / that they are under 2 weight sections / an olefin] worsens, the adaptability to various adherends falls, and thermal resistance will fall if 30 weight sections are exceeded, it is limited to the above-mentioned range. It is 5 - 20 weight section preferably.

[0029] The isocyanate prepolymers which will not be limited as an isocyanate cross-linking agent (C) especially if it has two or more isocyanate radicals in a molecule, for example, polyols, such as trimethylol propane and pentaerythritol, and the poly isocyanates, such as TORIECHI range isocyanate, diphenylmethane diisocyanate, and hexamethylene di-isocyanate, are made to react on the conditions that an isocyanate radical is superfluous, and are obtained are mentioned. Specifically, the Sumitomo Bayer urethane company make, Coronate L, isocyanate 0817, Sumi Joule N-3500, and Desmodur Z-4370 grade are mentioned.

[0030] The loadings of an isocyanate cross-linking agent (C) are 0.01 - 5 weight section to said acrylic (copolymer A) 100 weight section. Since bridge formation will progress too much, a gel molar fraction will exceed 50 % of the weight and the tuck and adhesion over polyethylene foam will decline if it becomes being under the 0.01 weight section constructing a bridge inadequate, thermal resistance falls and 5 weight sections are exceeded, it is limited to the above-mentioned range. It is 0.01 - 3 weight section preferably.

[0031] A softener, a plasticizer, a thickener, a CHIKUSO agent, an extending agent, a bulking agent, a pigment, a stabilizer, an antioxidant, an ultraviolet ray absorbent, a rusr-proofer, etc. may be blended with the binder constituent of this invention if needed in the range which does not check the effectiveness of this invention.

[0032] The binder constituent of this invention 1 **** adhesion which was excellent to porosity base materials, such as urethane foam with large expansion ratio, without being able to lower the elastic modulus in ordinary temperature, without lowering a hot elastic modulus not much, and reducing thermal resistance and creep resistance by that cause, since the tackifier whose softening temperature is 120-145 degrees C is blended with the acrylic copolymer of the structure in which the polymerization nature polymer segment whose glass transition temperature is -30 degrees C or less carried out graft polymerization. Moreover, since the bridge is moderately constructed with the isocyanate cross-linking agent, the outstanding thermal resistance and creep resistance are ****(ed).

[0033] The softening temperature of the rosin ester system tackifier (B-1) used by this invention 2 is 120-160 degrees C. Since the elastic modulus of the binder constituent in ordinary temperature will become high and the adhesion to a foam base material will fall if the elastic modulus of a binder constituent [in / that it is less than 120 degrees C / an elevated temperature] is low, and thermal resistance is bad and exceeds 160 degrees C, it is limited to the above-mentioned range. It is 125-150 degrees C preferably.

[0034] It is not limited especially as a rosin ester system tackifier (B-1), but the ester of derivatives, such as resin acid, such as an abietic acid, or a dimer of those, a disproportionation object, and a water garnish, a glycerol, pentaerythritol, etc., etc. is mentioned. For example, super ester A100 (the Arakawa chemical-industry company make, 100 degrees C of softening temperatures), super ester A115 (the Arakawa chemical-industry company make, 115 degrees C of softening temperatures), super ester A125 (the Arakawa chemical-industry company make, 125 degrees C of softening temperatures), the pen cel D125 (the Arakawa chemical-industry company make, 125 degrees C of softening temperatures), the pen cel D135 (the Arakawa chemical-industry company make, 135 degrees C of softening temperatures) the pen cel D160 (the Arakawa chemical-industry company make, 160 degrees C of softening temperatures), etc. be mentioned These resin may be used independently and may use two or more kinds together. When using two or more kinds together, average softening temperature (formula: sigma (softening temperature x number of copies)/sigma number of copies) should just be in the above-

mentioned range.

[0035] The loadings of a rosin ester system tackifier (B-1) are 2 - 20 weight section to the above-mentioned (copolymer A) 100 weight section. [acrylic] Since adhesion [as opposed to / that they are under 2 weight sections / an olefin] worsens, the adaptability to various adherends falls, and thermal resistance will fall if 20 weight sections are exceeded, it is limited to the above-mentioned range. It is 5 - 15 weight section preferably.

[0036] As a liquefied tackifier (B-2), especially if liquefied at ordinary temperature and ordinary pressure, it will not be limited, for example, rosin ester system resin, terpene phenol system resin, xylene-formaldehyde system resin, etc. are mentioned, and rosin ester system resin is used suitably especially, for example, super ester L (the Arakawa chemical-industry company make) -- a stevedore -- light ester 3 (Hercules make) etc. is mentioned.

[0037] The loadings of a liquefied tackifier (B-2) are 0.1 - 5 weight section to the acrylic (copolymer A) 100 weight section. Since thermal resistance will fall if adhesion [as opposed to / that it is under the 0.1 weight section / a foam base material] is inadequate and 5 weight sections are exceeded, it is limited to the above-mentioned range. It is 0.5 - 3 weight section preferably.

[0038] In the binder constituent of this invention 2, the class of the acrylic (copolymer A) acrylic-acid (meta) alkyl ester monomer (X-1), a vinyl system monomer (X-2), a polymerization nature polymer, a vinyl system monomer (X-3), and the above-mentioned isocyanate cross-linking agent (C) and the presentation are the same as that of what was explained in full detail by this invention 1.

[0039] The binder constituent of this invention 2 to the acrylic copolymer of the structure in which the non-polymerization nature polymer segment whose glass transition temperature is -30 degrees C or less carried out graft polymerization Since optimum dose combination of the rosin ester system tackifier and liquefied tackifier whose softening temperature is 120-160 degrees C is carried out, respectively Adhesion which was excellent to porosity base materials, such as urethane foam with large expansion ratio, is ****(ed) without being able to lower the elastic modulus in ordinary temperature and reducing thermal resistance and creep resistance by that cause, setting up a hot elastic modulus low. Moreover, the thermal resistance and creep resistance which were excellent since the bridge was moderately constructed with the isocyanate cross-linking agent are ****(ed).

[0040] As a peroxide (Z) which has two or more peroxy association in the monad as an initiator used for the polymerization of an acrylic copolymer (A) with the binder constituent of this invention 3 For example, 2, the 5-dimethyl -2, 5-JI (2-ethylhexyl peroxy) hexane, 1 and 1-screw (t-hexyl peroxy) - 3, 3, a 5-trimethyl cyclohexane, The 1 and 1-screw (t-hexyl peroxy) cyclohexane, 1, and 1-screws (t-butylperoxy) 3 and 3, a 5-trimethyl cyclohexane, 1 and 1-screw (t-butylperoxy) cyclohexane, 1, and 1-screw (t-butylperoxy) cyclo dodecane, 2, the 5-dimethyl -2, 5-(m-tolyl peroxy) hexane, 2, the 5-dimethyl -2, 5-JI (benzoyl peroxy) hexane, 2 and 2-screw (t-butylperoxy) butane, n-butyl -4, 4-screw (t-butylperoxy) valerate, A 2 and 2-screw (4 and 4-G t-butylperoxy cyclohexyl) propane, 1, and 1-G t-butylperoxy-2-methylcyclohexane, [0041] A G t-butylperoxy trimethyl horse mackerel peat, screw (t-butylperoxy)-alpha-n-butyl SUBERETO, screw (t-amyl peroxy)-alpha-n-butyl SUBERETO, screw (t-hexyl peroxy)-alpha-n-butyl SUBERETO, screw (1, 1, 3, and 3-tetramethylbutylperoxy)-alpha-n-butyl SUBERETO, JIKUMIRU peroxy-alpha-n-butyl SUBERETO, etc. are mentioned.

[0042] Since a block copolymer is easy to be obtained by the two-step polymerization and it excels also in the thermal resistance of a binder constituent, and the adhesion to a foam base material when what has two or more kinds of peroxy association from which decomposition temperature differs among the above is used, it is desirable. Have suitably peroxy association from which 10 degrees C or more of reduction-by-half temperature differ for 10 hours. A 1 and 1-G t-butylperoxy-2-methylcyclohexane, a G t-butylperoxy trimethyl horse mackerel peat, Screw (t-butylperoxy)-alpha-n-butyl SUBERETO, screw (t-amino peroxy)-alpha-n-butyl SUBERETO, Screw (t-hexyl peroxy)-alpha-n-butyl SUBERETO, screw (1, 1, 3, and 3-tetramethylbutylperoxy)-alpha-n-butyl SUBERETO, and JIKUMIRU peroxy-alpha-n-butyl SUBERETO are used.

[0043] It is the same as the acrylic-acid (meta) alkyl ester monomer (X-1) which constitutes monomer mixture (X), a vinyl system monomer (X-2), and (X-3) the thing stated by said this invention 1.

[0044] As for the acrylic-acid alkyl ester monomer (Y-1) which constitutes monomer mixture (Y) and whose glass transition temperature is -30 degrees C or less (meta), the same thing of a monomer (Y-1) and the vinyl system monomer (Y-2) in which radical copolymerization is possible as the above-mentioned monomer (X-1) is the same as that of the above-mentioned vinyl system monomer (X-3) again.

[0045] Although especially the approach of the radical copolymerization in a two-step polymerization is not limited, since combination and coating of a binder constituent are usually performed in the state of a solution, a solution polymerization method is suitable for them. It is not limited especially as a solvent used by solution polymerization, for example, alicycle group system solvents [, such as an aliphatic series system solvent; cyclohexane,], such as acetic-ester system solvent; n-hexanes, such as ketones; methyl acetate, such as aromatic solvent; acetones, such as benzene, toluene, and a xylene, and a methyl ethyl ketone, ethyl acetate, and butyl acetate, and n-heptane, etc. are used.

[0046] In order to adjust molecular weight in solution polymerization, a suitable chain transfer agent may be used. As a chain transfer agent, dodecyl mercaptan etc. is mentioned, for example. In this case, as for the weight average molecular weight of an acrylic copolymer (A), it is desirable to make it set to 300,000-2 million. Cohesive force is insufficient in it being less than 30, thermal resistance and creep resistance fall, and since the viscosity of a binder solution will become high too much if 2 million is exceeded, coating nature falls.

[0047] As for the binder constituent of this inventions 1-3, it is desirable that the rate of insoluble matter to ethyl acetate (gel molar fraction) is 20 - 50 % of the weight. This reason is that it becomes what the adhesion over thermal resistance and a foam base material, especially polyethylene foam and adhesion were secured.

[0048] Gel here points out the insoluble matter to the ethyl acetate of a binder. Carry out coating so that the thickness after drying a binder constituent solution to the mold release side of a release paper may be set to 65 micrometers, and it is made to dry for 5 minutes in a 80-degree C drier, and it is recuperated for one week on condition that 20 degrees C and 60%RH in what stuck the mold release side of a release paper on the binder coating side further. Thus, it is the weight of the obtained binder W1 It carries out. It is weight, although it filtered with the stainless steel network of 180 meshes, the insoluble matter which remained in the network was dried in the 80-degree C drier for 3 hours and ethyl acetate was completely volatilized, after being immersed in ethyl acetate and making this **** for three days W2 It carries out. A gel molar fraction is the value acquired by the degree type.

Gel molar fraction (% of the weight) = $(W2 / W1) \times 100$

[0049] Bridge formation is inadequate in the above-mentioned gel molar fraction being less than 20 % of the weight, thermal resistance falls, if it exceeds 50 % of the weight, bridge formation will progress too much, adhesion with polyethylene foam will fall, and a tuck and adhesion will decline. It is 25 - 45 % of the weight preferably.

[0050] A softener, a plasticizer, a thickener, a CHIKUSO agent, an extending agent, a bulking agent, a pigment, a stabilizer, an antioxidant, an ultraviolet ray absorbent, a rust-proofer, etc. may be blended with the binder constituent of this invention if needed in the range which does not check the effectiveness of this invention.

[0051] It may come to carry out the laminating of at least one sort of this invention 1 thru/or the binder constituent of 4 to a front face, and the adhesion workpieces of this invention 5 may be things, such as one side adhesive tape, a pressure sensitive double coated tape, foam adhesive tape, and a pressure sensitive adhesive sheet, and may be the adhesion film or sheet which consists of the binder constituent itself obtained on a release paper by carrying out coating of at least one sort of the binder constituent of this invention, for example, without using a base material.

[0052] It is not limited especially as a class of the above-mentioned base material, for example, various rubber system foam, such as various plastics foam; natural rubber foam, such as various nonwoven fabric; polyethylene foam, such as various film; rayon systems, such as cellophane, polyethylene, polypropylene, polyester, and polystyrene, and a cellulose system, polypropylene foam, and polyurethane foam, styrene-butadiene-rubber foam, chloroprene rubber foam, and acrylonitrile-butadiene rubber foam, etc. is mentioned.

[0053] When creating an adhesion workpiece using the above-mentioned base material In order to raise further the adhesion of the binder constituent of this invention to a base material, beforehand a binder constituent to the base material side (coating side) which should be carried out coating Corona discharge treatment, In order to raise the mold-release characteristic (expansion nature) of the binder constituent from the base material side (henceforth a "non-coating side") which may perform surface treatment, such as primer coating, and does not carry out coating of the binder constituent, mold release processing may be beforehand performed to the non-coating side of a base material.

[0054] The approach of carrying out the laminating of the binder constituent to a base material has the approach of applying directly using a roll coater, a bar coating machine, a flow coater, a spray coater, a doctor blade, etc., the approach of imprinting the formed binder layer which carried out spreading desiccation to a release paper, etc. that what is necessary is just to use the approach usually performed.

[0055] Although the thickness of the binder constituent by which a laminating is carried out is not limited especially, generally its about 10-200 micrometers are [that what is necessary is to just be suitably chosen according to the purpose of the adhesion workpiece obtained an application, etc.] desirable at the thickness after desiccation.

[0056] When an adhesion workpiece is the thing which comes to carry out coating of the binder constituent to both sides of a base material, the binder constituent by which coating is carried out to each field may be the same presentation, and may differ.

[0057] although the thing or base material which uses a base material is not used for the above-mentioned adhesion workpiece -- any case -- one kind of binder constituent -- a monolayer -- or two or more layer laminating may be carried out, and two or more layer laminating of two or more kinds of binder constituents may be carried out.

[0058] Since it comes to carry out the laminating of the binder constituent of this invention, the adhesion workpiece of this invention 3 is excellent in thermal resistance and creep resistance, having the adhesion to the outstanding foam base material, and is used suitable for the extensive purpose and an application.

[0059]

[Embodiment of the Invention]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples.

[0060] (Examples 1-9 and examples 1-7 of a comparison)

(1) After teaching and carrying out the temperature up of the monomers of the presentation shown in Table 1 and 2, a polymerization nature polymer, and the ethyl-acetate 81.8 weight section to the four-lot flask equipped with the polymerization agitator, the reflux cooling pipe, dropping funnel, and thermometer of an acrylic copolymer and making it flow back for 30 minutes, the benzoyl peroxide 0.1 weight section was dropped at it, and it was made to react to it for 7 hours. Subsequently, the benzoyl peroxide 0.1 weight section was dropped and it was made to react for 3 hours. The toluene 40.4 weight section was added after that, it cooled, and the acrylic copolymer solution of 45% of solid content was obtained.

[0061] (2) after carrying out addition mixing of the tackifier and liquefied tackifier of a presentation which were shown in Table 1 and 2 and diluting with toluene further in the preparation profit **** acrylic copolymer solution of a binder constituent at 40% of solid content, addition mixing of the cross linking agent shown in Table 1 and 2 was carried out, and the binder constituent solution was obtained.

[0062] (3) After carrying out coating of the creation above-mentioned binder constituent solution of foam adhesive tape so that the thickness after drying to the mold release side of a release paper may be set to 65 micrometers using a doctor blade, it was dried for 5 minutes in the 80-degree C dryer. Subsequently, using the sticking-by-pressure roller, the desiccation coat of a binder constituent was made to stick on an urethane system foam base material with a thickness of 10mm mutually, it was stuck by pressure, it was recuperated for one week by 20 degrees C and 65%RH, and foam adhesive tape was obtained.

[0063] (Examples 10-20 and examples 8-16 of a comparison)

(1) After teaching the monomer mixture of the ethyl-acetate 53.3 weight section and the first stage eye

shown in Table 3 to the polymerization agitator of an acrylic copolymer (A), a reflux cooling pipe, a thermometer, and the four-lot flask equipped with nitrogen entrainment Rhine and carrying out a temperature up to them to predetermined temperature under a nitrogen purge, the predetermined polymerization initiator was added and the predetermined time reaction was carried out. Subsequently, the monomer mixture of the second stage eye which carried out the temperature up to predetermined temperature and which was shown in Table 3 was added, and the predetermined time polymerization reaction was continued. Then, the toluene 96.7 weight section was added, it cooled, and the acrylic copolymer (A) solution of 40% of solid content was obtained.

[0064] (2) After carrying out addition mixing of the tackifier and liquefied tackifier of a presentation which were shown in the production above-mentioned acrylic copolymer (A) solution of a binder constituent and foam adhesive tape in Table 4 and 5 and diluting with toluene to 40% of solid content further, addition mixing of the cross linking agent shown in Table 4 and 5 was carried out, and the binder constituent solution was obtained. Foam adhesive tape was produced like examples 1-9 using this binder constituent solution.

[0065] After sticking on the SUS plate by having made the foam adhesive tape of evaluation (80-degree-C exfoliation holding power) each example and each example of a comparison into width of face of 25mm and sticking 1 ***** of 2kg rollers by pressure, it was recuperated by 20 degrees C and 65% RH on the 1st. Subsequently, after constructing a 50g static load as a foam adhesive tape side turns down within this oven after leaving it in 80-degree C oven for 30 minutes, and leaving it for 1 hour, the existence of fall by exfoliation was checked, and when having not fallen, exfoliation die length was measured. The example was shown in Table 1 and Table 4, and the above result was shown in Table 2 and Table 5 about the example of a comparison.

[0066]

[Table 1]

		実施例								
		1	2	3	4	5	6	7	8	9
モノマー組成	アクリル酸ブチル			52			89			
	アクリル酸2-エチルヘキシル			40			—			
	アクリル酸2-ヒドロキシエチル			0.3			0.05			
	重合性ポリメタクリル酸ブチル			5			8			
	アクリル酸			2.7			2.95			
粘着性	ロジンエステル1(軟化点100℃)※1	10	—	—	—	—	—	10	—	—
	ロジンエステル2(軟化点125℃)※2	—	5	10	—	8	5	—	5	—
	ロジンエステル3(軟化点125℃)※3	—	—	—	5	—	—	—	—	5
	ロジンエステル4(軟化点135℃)※4	—	5	—	5	8	5	—	5	—
	ロジンエステル5(軟化点160℃)※5	10	—	5	—	—	—	10	—	5
	石油樹脂(融点125℃)※6	—	—	—	—	—	5	—	—	—
	平均軟化点(℃)	130	130	137	130	130	128	130	130	143
被膜粘着付与滑脂		※7	—	—	—	—	—	0.5	1.0	2.0
架橋剤 イソシアネートプレポリマー		※8	1.0	0.8	0.8	1.4	3.0	0.8	1.0	0.8
物性	8.0℃剥離保持力 (剥離長さmm)	ウレタン系接着剤	5	5	7	5	3	7	2	2
	ポリエチレン系接着剤	5	5	3	4	3.5	5	5	3	3
	ゲル分率(質量%)	40	40	30	40	45	35	35	35	35

[0067]

[Table 2]

		比較例								
		1	2	3	4	5	6	7	8	9
モノマー組成	アクリル酸ブチル	57	52		57		52			
	アクリル酸2-エチルヘキシル				40					
	アクリル酸2-ヒドロキシエチル		0.3		-	0.3	-	0.3	0.7	0.3
	重合性ポリメタクリル酸ブチル	-		5		-		5		
	アクリル酸		2.7		3.0	2.7	3.0	2.7	2.3	2.7
接着付着樹脂	ロジンエステル1(軟化点100°C)※1	10	20	-	10	10	10	-	10	10
	ロジンエステル2(軟化点125°C)※2	-	-	-	-	-	-	-	-	-
	ロジンエステル3(軟化点125°C)※3	-	-	-	-	-	-	-	-	-
	ロジンエステル4(軟化点135°C)※4	-	-	-	-	-	-	-	-	-
	ロジンエステル5(軟化点160°C)※5	10	-	10	10	10	10	-	10	10
	石油樹脂(融点125°C)※6	-	-	-	-	-	-	20	-	-
	平均軟化点(°C)	130	100	160	130	130	130	125	130	130
液体接着付着樹脂		※7	-	-	-	0.5	1.0	2.0	-	-
架橋剤 イソシアネートプレポリマー※8		1.0	1.0	1.0	-	1.0	-	1.4	1.0	5
物性	8.0°C時強度保持力 (引張長さmm)	ウレタン系接着剤	*落下	落下	*落下	落下	*落下	落下	5	5
	ポリエチレン系接着剤	5	*落下	*落下	落下	*落下	落下	*落下	*落下	*落下
	ゲル分率(重量%)	40	40	35	0	35	0	40	80	60

[0068]

[Table 3]

アクリル系共重合体(A)		A-1	A-2	A-3	A-4	A-5	A-6	A-7		
重合開始剤	1	0.3	0.3	0.4	0.3	-	0.3	0.3		
	2	-	-	-	-	0.3	-	-		
一段目重合	仕込み量(重量部)		80	20	10	20	80	100	80	
	重	X-1	アクリル酸ブチル	57	100	100	50	57	57	
	モ	X-2	アクリル酸2-エチルヘキシル	40	-	-	49.6	40	40	
	ノ	X-3	アクリル酸2-ヒドロキシエチル	0.3	-	-	0.4	0.3	0.3	
	マ		アクリル酸	2.7	-	-	-	2.7	3.0	
	ー		ドデシルメルカプタン	0.05	0.05	0.05	0.05	0.05	0.05	
	段		ガラス転移温度(°C)	-	-54	-54	-70	-	-	
	目		重合温度(°C)	75	75	75	75	75	75	
二段目重合	反応時間(hrs)		4	4	4	4	4	10	4	
	混	Y-1	仕込み量(重量部)	20	80	80	80	20	-	20
	合	Y-2	アクリル酸ブチル	100	57	57	87	100	-	100
	重		アクリル酸2-エチルヘキシル	-	40	40	30	-	-	-
	モ		アクリル酸2-ヒドロキシエチル	-	0.3	0.3	0.3	-	-	-
	ノ		アクリル酸	-	2.7	2.7	2.7	-	-	-
	マ		ドデシルメルカプタン	0.05	0.05	0.05	0.05	0.05	0.05	0.05
	ー		ガラス転移温度(°C)	-54	-	-	-	-54	-	-54
重合温度(°C)		85	85	88	85	85	-	85		
反応時間(hrs)		6	6	6	6	6	-	6		

[0069]

[Table 4]

		実施例										
		10	11	12	13	14	15	16	17	18	19	20
アクリル系共重合体(A)	A-1	100	100	100	100	100	100	100	100	-	-	-
	A-2	-	-	-	-	-	-	-	-	100	-	-
	A-3	-	-	-	-	-	-	-	-	-	100	-
	A-4	-	-	-	-	-	-	-	-	-	-	100
	A-5	-	-	-	-	-	-	-	-	-	-	-
	A-6	-	-	-	-	-	-	-	-	-	-	-
	A-7	-	-	-	-	-	-	-	-	-	-	-
粘着剤 与接着剤	ロジンエステル1 (軟化点100℃) ※1	10	-	-	-	-	10	-	-	10	10	10
	ロジンエステル2 (軟化点125℃) ※2	-	5	10	-	5	-	5	-	-	-	-
	ロジンエステル3 (軟化点125℃) ※3	-	-	-	5	-	-	-	5	-	-	-
	ロジンエステル4 (軟化点135℃) ※4	-	5	-	5	5	-	5	-	-	-	-
	ロジンエステル5 (軟化点160℃) ※5	10	-	5	-	-	10	-	5	10	10	10
	石蜡油 (融点125℃) ※6	-	-	-	-	5	-	-	-	-	-	-
	軟化点 (℃)	130	130	137	130	128	130	130	143	130	130	130
被覆剤 与接着剤		※7	-	-	-	-	0.5	1.0	2.0	-	-	-
架橋剤 イソシアネートプレポリマー		※8	1.0	0.8	0.8	1.4	0.8	1.0	0.8	1.4	1.0	1.0
物性	ウレタンの溶融軟化点 80℃耐熱強度 (引張強さmm)	7	9	8	7	9	5	3	3	6	7	12

[0070]

[Table 5]

		比較例									
		10	11	12	13	14	15	16	17	18	
アクリル系共重合体(A)	A-1	-	-	-	100	100	100	100	-	-	
	A-2	-	-	-	-	-	-	-	-	-	
	A-3	-	-	-	-	-	-	-	-	-	
	A-4	-	-	-	-	-	-	-	-	-	
	A-5	100	-	100	-	-	-	-	-	-	
	A-6	-	100	-	-	-	-	-	-	-	
	A-7	-	-	-	-	-	-	-	100	100	
粘着剤 与接着剤	ロジンエステル1 (軟化点100℃) ※1	10	10	10	20	-	10	-	10	10	
	ロジンエステル2 (軟化点125℃) ※2	-	-	-	-	-	-	-	-	-	
	ロジンエステル3 (軟化点125℃) ※3	-	-	-	-	-	-	-	-	-	
	ロジンエステル4 (軟化点135℃) ※4	-	-	-	-	-	-	-	-	-	
	ロジンエステル5 (軟化点160℃) ※5	10	10	10	-	10	10	-	10	10	
	石蜡油 (融点125℃) ※6	-	-	-	-	-	-	20	-	-	
	軟化点 (℃)	130	130	130	100	180	130	125	130	130	
被覆剤 与接着剤		※7	-	-	0.5	-	-	-	-	2.0	
架橋剤 イソシアネートプレポリマー		※8	1.0	1.0	1.0	1.0	1.0	-	1.0	1.0	1.4
物性	ウレタンの溶融軟化点 80℃耐熱強度 (引張強さmm)	60	*落下	50	*落下	*落下	落下	*落下	70	75	

[0071] [Note] Units other than physical properties are the weight sections.

* : it exfoliated in the foam interface.

**1: The Arakawa chemical-industry company make (100 degrees C of softening temperatures, trade name "super ester A100")

**2: The Arakawa chemical-industry company make (125 degrees C of softening temperatures, trade name "super ester A125")

**3: The Arakawa chemical-industry company make (125 degrees C of softening temperatures, trade

name "the pen cel D125")

**4: The Arakawa chemical-industry company make (135 degrees C of softening temperatures, trade name "the pen cel D135")

**5: The Arakawa chemical-industry company make (160 degrees C of softening temperatures, trade name "the pen cel D160")

**6: Mitsui Petrochemical Industries, Ltd. make (the melting point of 125 degrees C, trade name "FTR6125")

**7: the Hercules make (a trade name -- "-- a stevedore -- light ester 3")

**8: What has the Sumitomo Bayer urethane company make and three isocyanate radicals (trade name "coronate L55")

[0072]

[Effect of the Invention] Since the binder constituent of invention is as above-mentioned, it excels in the adhesion over a porosity base material with high expansion ratio, such as urethane foam and polyethylene foam, and excels in thermal resistance and creep resistance, and the adhesion workpiece with which coating of this binder constituent was carried out is used suitable for the extensive purposes, such as building materials and home electronics, and an application.

[Translation done.]